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# Kinetic studies of thermal degradation of natural cellulosic materials

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## Abstract

The thermal degradation behaviors of various wood species have been studied from 200° to 650°C by TG and DTG in an atmosphere of nitrogen. The data show a complex pattern of overlapping DTG peaks. This is in contrast to $\alpha$-cellulose thermal degradations. It is demonstrated that computer simulations can describe all the patterns of behavior on the basis of two overlapping mechanisms, differing in their reaction order and Arrhenius parameters. It is emphasized that, although such simulations can be drawn up on a computer, there are an infinite number of solutions to two overlapping peaks. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Wood species; Rising temperature thermal analysis; Computer simulation

## 1. Introduction

The thermal degradation of natural cellulosic materials in nitrogen at one atmosphere occurs through a series of complex chemical reactions, which poses problems in evaluating the mechanism of pyrolysis. There are extensive publications dealing with the kinetic study of thermal degradation of cellulose, but less attention is paid to the kinetics of degradation of the more complex system – natural cellulosic materials, such as wood species [1–3]. The thermal analysis data and attempts at kinetic evaluation show that the system is complicated by the presence of overlapping reaction sequences. Various reaction sequences have been suggested, all of them involving a degradation step to levoglucosan, and the subsequent breakdown of this material to other simpler organic species. These is, however, no suggestion as to the further progression of the breakdown to amorphous carbon, the observed end product of degradation [4]. In earlier reports, it was shown that the progress of this complicated sequence is rate governed by phase boundary conditions and probably by diffusion processes [5]. There is the probability that these processes are rate-determining and this simplifies somewhat the kinetic interpretation.

In the present study, the authors demonstrate that the application of a single reaction mechanism to the reaction sequence for natural cellulosic systems is, at best, only able to describe a portion of the overall degradation process. The kinetic analysis is carried out by interpreting the experimental data by the use of the derivative as well as the integrated methods. The kinetic mechanism and the Arrhenius parameters thus calculated can then be used to reconstruct the thermal analysis data. Such theoretical data can then be directly compared against the experimental data to reinforce the point that such attempts only provide a limited agreement over a portion of the entire degradation process. A mathematical simulation is utilized, however, to demonstrate that the type of overlapping reaction sequence can be modeled on the basis of two kinetic processes occurring sequentially.

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## 2. Experimental

Seven wood species were investigated. They were supplied by a local timber supplier and are named from the type of tree from which they are obtained: spruce, hardmaple, ash, softmaple, basswood, red oak, and poplar. They were supplied as saw dust. For the purpose of experiment, they are crushed at room temperature and then passed through a 40 μm sieve.

The thermal analysis equipment consists of a simultaneous TGA-DTA 2960 unit from TA instruments. The samples were placed in a platinum crucible, with an empty platinum crucible as a reference, and the sample size ranges from 11 to 18 mg. A heating rate of 10°C/min was used during all the experiments. The samples were analyzed in dry nitrogen at a gas flow rate of 100 ml/min.

Quick Basic was used to write up the programs. The data from Quick Basic were transformed to Excel format file to draw the graphics.

## 3. Results and discussion

In solid-state kinetic analysis, it is convenient to express the reaction sequence in terms of the reaction extent, $\alpha$, defined as:

$$\alpha = \frac{(w_\mathrm{i} - w)}{w_\mathrm{i} - w_\mathrm{f}} \tag{1}$$

where $w$ is the weight or weight percentage of a sample at a certain time, $w_\mathrm{i}$ and $w_\mathrm{f}$ the initial and final values of the reaction.

The reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ in the derivative form is given by:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = f(\alpha)k(T) \tag{2}$$

Here, $f(\alpha)$ is a function of $\alpha$ which represents the reaction mechanism, as listed in Table 1 of Ref. [6].

The Arrhenius parameters, $E_\mathrm{a}$ the activation energy and the pre-exponential factor, $A$, can be calculated using:

$$k(T) = A\exp(-E_\mathrm{a}/RT) \tag{3}$$

where $R$ is the gas constant, and $T$ the absolute temperature. If rising-temperature experiments are performed, then the $\alpha$ vs. $T$ plot can be derived. If Eq. (2) is combined with Eq. (3), then

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = A\exp(-E_\mathrm{a}/RT)f(\alpha)/\beta \tag{4}$$

or

$$\frac{\mathrm{d}\alpha}{f(\alpha)} = A\exp(-E_\mathrm{a}/RT)\mathrm{d}T/\beta \tag{5}$$

where $\beta$ is the heating rate, i.e. $\mathrm{d}T/\mathrm{d}t$. Eq. (4) provides the basis for a derivative method to obtain $A$, $E_\mathrm{a}$ via linear regression; while Eq. (5) can be integrated to

$$G(\alpha) \equiv \int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_f} \exp(-E_\mathrm{a}/RT)\mathrm{d}T \tag{6}$$

The approximation to this integration used in the present study is proposed by Madhusudanan [7]:

$$\ln\left(\frac{G(\alpha)}{T^{1.921503}}\right) = \ln(AE_\mathrm{a}/\beta R) + 3.7720501 - 1.921503\ln E_\mathrm{a} - E_\mathrm{a}/RT \tag{7}$$

Different integral forms of $G(\alpha)$ are also listed in Table 1 of Ref. [5].

The derivative method is applied to the thermal degradation of various wood species. To determine the most probable mechanism, all these 23 $f(\alpha)$ functions have been tried. The most probable mechanism is chosen mainly according to $R^2$, the regression factor. This should not be the only factor in choosing a most probable kinetic mechanism and, in particular, the fibrous and cellular natural, out of the cellulosic material must also be taken into account. The temperature range in which analysis is determined is from 200° to 400°C, with points being noted every 2°C.

It is found that most of wood species degraded between 200° and 400°C via a B1 mechanism, i.e. Prout–Tompkins equation, as shown in Table 1. In certain instances, a D3, F1 or R3 mechanism gave a best fit.

There are, thus, various methods of continued analysis available. These include:

1. compare $R^2$ after including more data points, for example, every 1°C;
2. coupled with other methods, such as Friedman or Ozawa method to compare the closeness of $A$ and $E_\mathrm{a}$ to one of these probable mechanisms;

Table 1
Details of the kinetic studies of thermal degradation of various wood species

| Wood species | Mechanism | | $R^2$ | $A(s^{-1})$ | $E_a$(kJ/mol) |
|---|---|---|---|---|---|
| Spruce | D3 | | 0.9921 | 3.97E10 | 163.73 |
| Hardmaple | B1 | $n=2$ | 0.9817 | 6.44E16 | 222.74 |
| | | $n=3$ | 0.9831 | 9.35E26 | 341.45 |
| | | $n=4$ | 0.9831 | 1.21E37 | 460.18 |
| Ash | B1 | $n=2$ | 0.9914 | 4.19E15 | 206.66 |
| | | $n=3$ | 0.9908 | 1.89E25 | 318.10 |
| | D3 | | 0.9802 | 1.70E12 | 182.37 |
| | F1 | | 0.9835 | 6.97E5 | 95.22 |
| Softmaple | B1 | $n=2$ | 0.9822 | 6.13E15 | 210.65 |
| | | $n=3$ | 0.9831 | 2.60E25 | 322.98 |
| | | $n=4$ | 0.9828 | 9.79E34 | 435.32 |
| | D3 | | 0.9820 | 5.60E12 | 189.82 |
| Basswood | B1 | $n=2$ | 0.9918 | 1.24E15 | 200.64 |
| | | $n=3$ | 0.9920 | 2.55E24 | 308.19 |
| | | $n=4$ | 0.9916 | 4.66E33 | 415.75 |
| | D3 | | 0.9860 | 5.12E11 | 176.42 |
| Red oak | B1 | $n=2$ | 0.9821 | 8.64E14 | 198.97 |
| | | $n=3$ | 0.9820 | 1.84E24 | 306.70 |
| | | $n=4$ | 0.9812 | 3.50E33 | 414.44 |
| Poplar | B1 | $n=2$ | 0.9860 | 4.48E16 | 220.64 |
| | | $n=3$ | 0.9859 | 5.25E26 | 338.17 |
| | | $n=4$ | 0.9854 | 5.48E36 | 455.70 |
| | R3 | | 0.9820 | 3.43E4 | 88.67 |
| | D3 | | 0.9821 | 3.99E13 | 199.70 |

3. use isothermal experiments to confirm $A$ and $E_a$ values; and
4. reconstruct the curve according to the $A$ and $E_a$ values obtained from derivative method, using the integral method.

In the present study, method 4 has been used on thermal degradation data of spruce and red oak.

Fig. 1 shows the thermogravimetric curve of the degradation of spruce from room temperature to 650°C and the corresponding experimental and theoretical data of spruce which degrades via D3 mechanism in the temperature range 200° to 400°C. It is found that there is deviation over the 330–360°C range, but in the 200–400°C range, the overall regression factor is 0.9921 for the equivalence of the experimental and theoretical data.

Fig. 2 shows the thermogravimetric curve of the degradation of red oak from room temperature to 650°C and the corresponding experimental and theoretical data for red oak which degrades via B1 mechanism in the 200–400°C range. There are three mechanisms with similar $R^2$ values. It is found that all three of these mechanisms show deviation between experimental and theoretical data from 220° to 370°C. In the 220–336°C range, the theoretical data are fewer than the experimental one. For the temperature range from 336° to 370°C, the opposite is true. Although all these data give reasonable regression factors, which indicate the closeness between experimental and theoretical data, the deviation from theoretical data reveals that one mechanism is insufficient to describe the degradation of complex natural cellulosic materials – wood species, unlike cellulose, whose mechanism has been studied intensively.

A computer model can be generated to simulate the experimental data based on the following assumptions:

1. there are two mechanisms for each thermal degradation process; and
2. each mechanism is a first-order reaction.

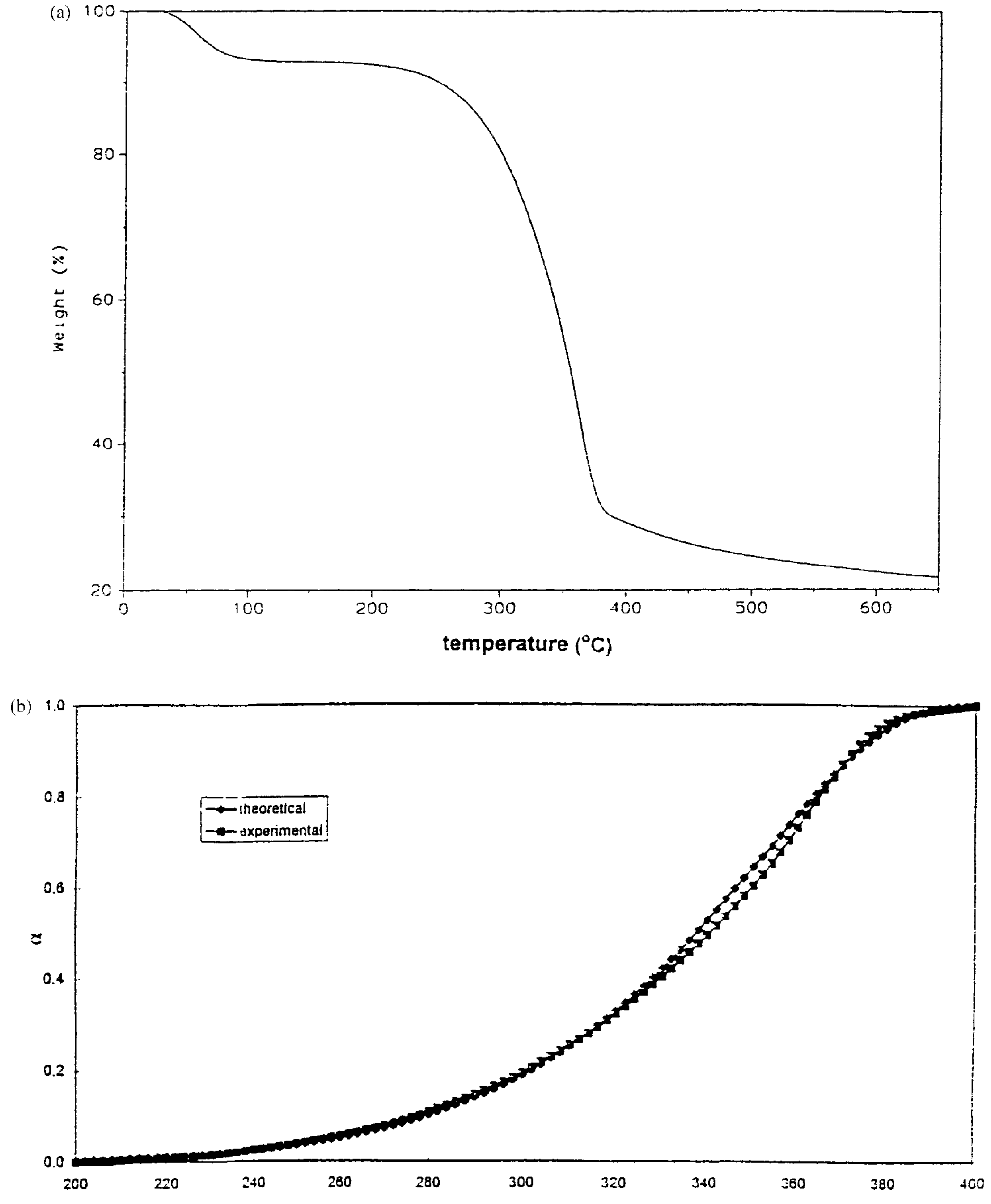


Fig. 1. (a) TG curve of spruce in flowing nitrogen from room temperature to 650°C, and (b) corresponding experimental and theoretical data via D3 mechanism in the 200–400°C range. $A$=3.97E10 $s^{-1}$, $E_a$=163.726 kJ/mol.

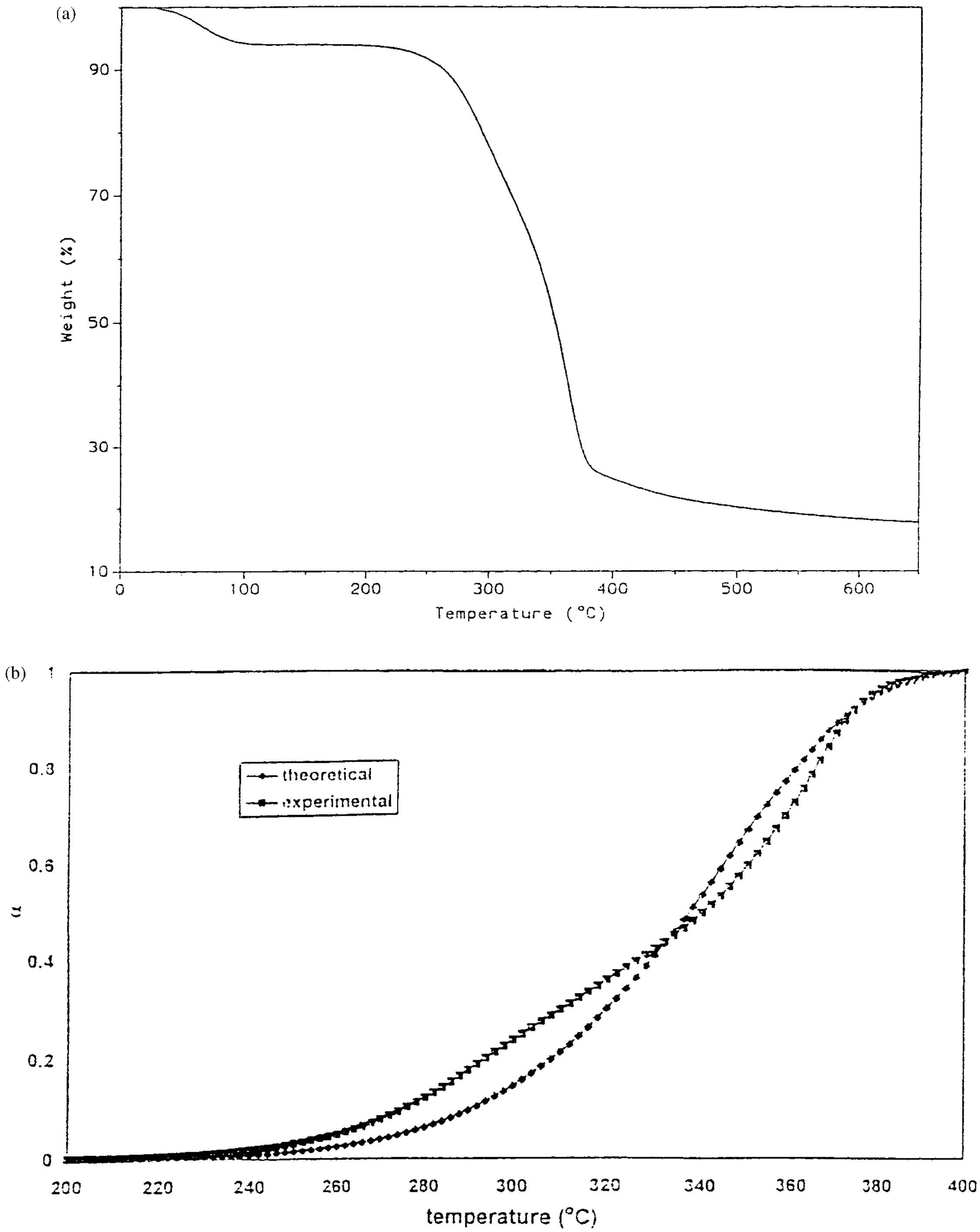
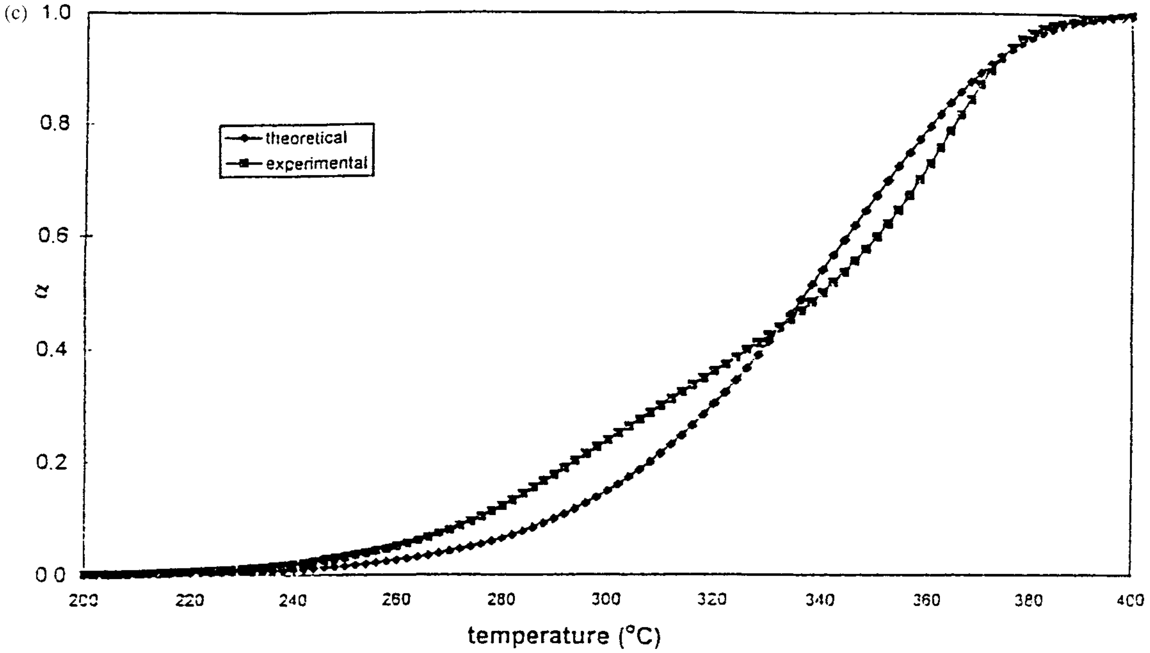


Fig. 2. (a) TG curve of red oak in flowing nitrogen from room temperature to 650°C; and corresponding experimental and theoretical data in the 200–400°C range. (b) B1 $n$=2, $A$=8.64E14 s$^{-1}$, $E_a$=198.967 kJ/mol; (c) B1 $n$=3, $A$=1.84E24 s$^{-1}$, $E_a$=306.702 kJ/mol (c); and (d) B1 $n$=4, $A$=3.50E33 s$^{-1}$, $E_a$=414.438 kJ/mol (d).



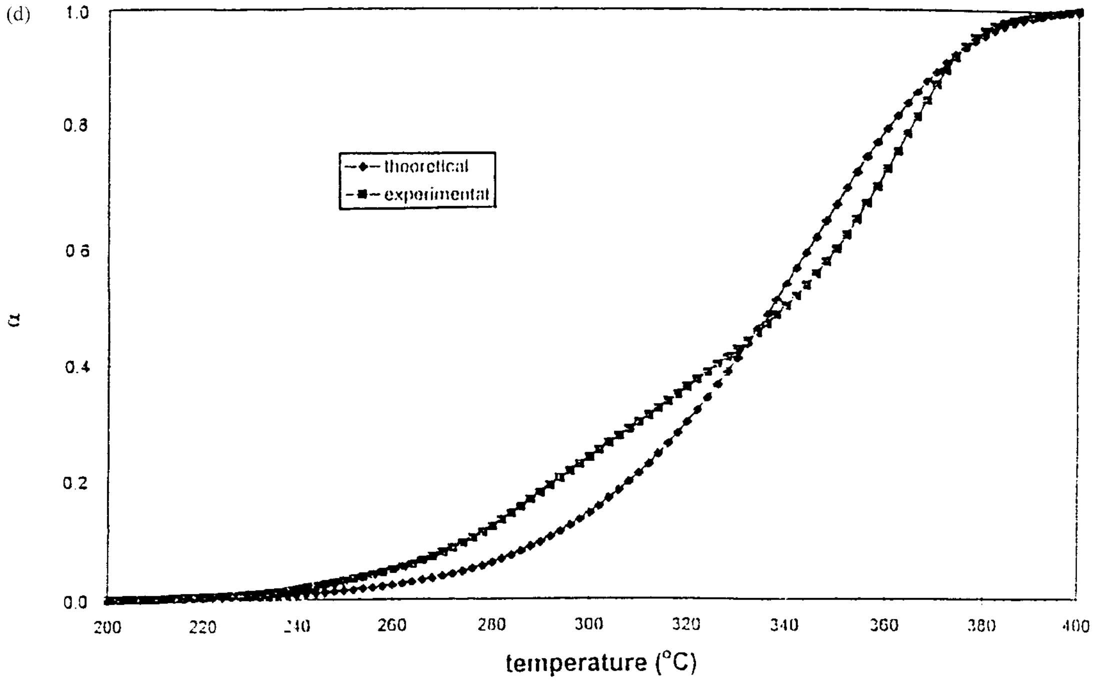


Fig. 2. (*Continued*)

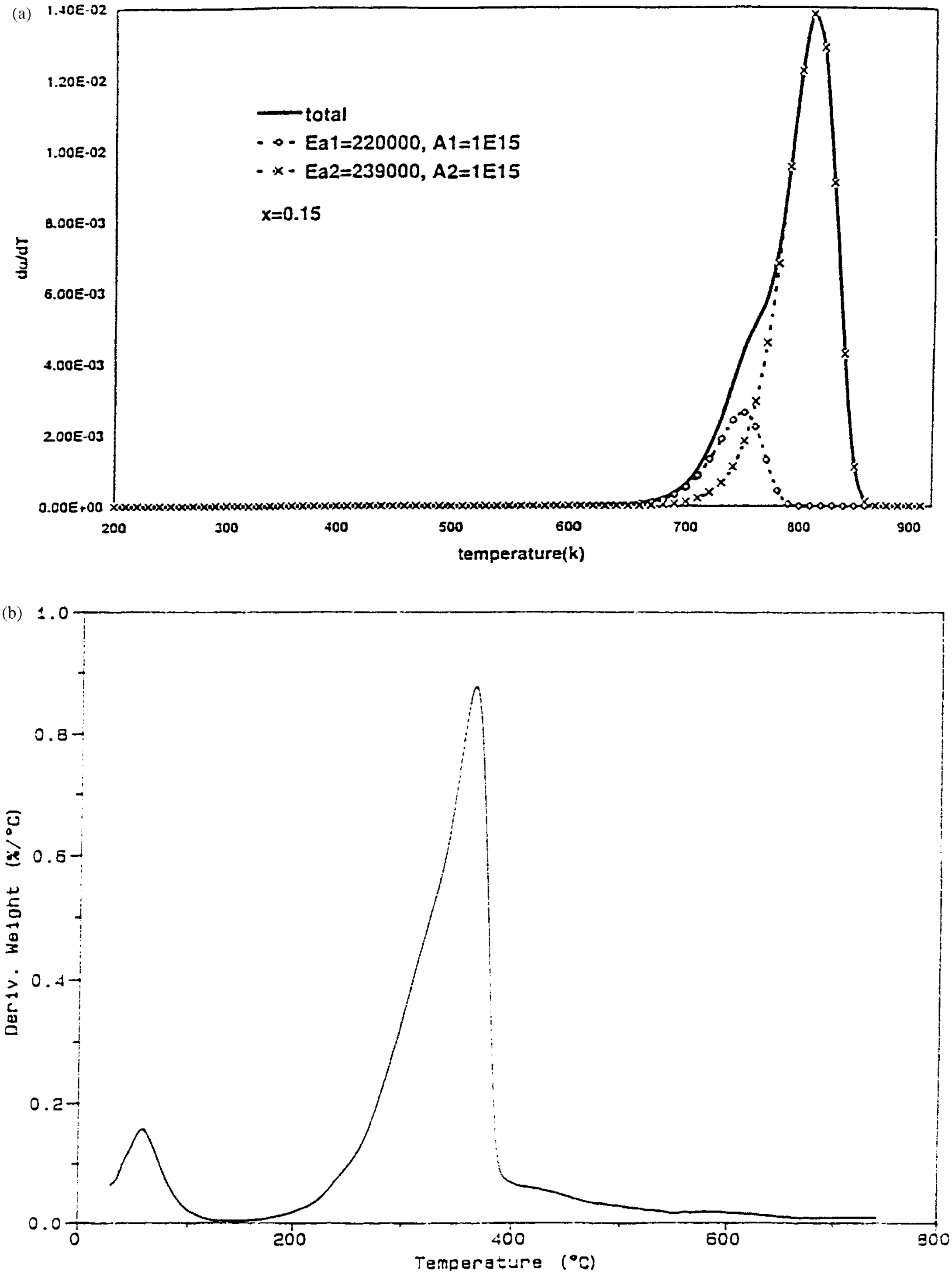


Fig. 3. Simulated and experimental DTG curves of spruce and red oak. (a) Simulated, and (b) experimental curves of spruce; and (c) simulated, and (d) experimental curves of red oak.

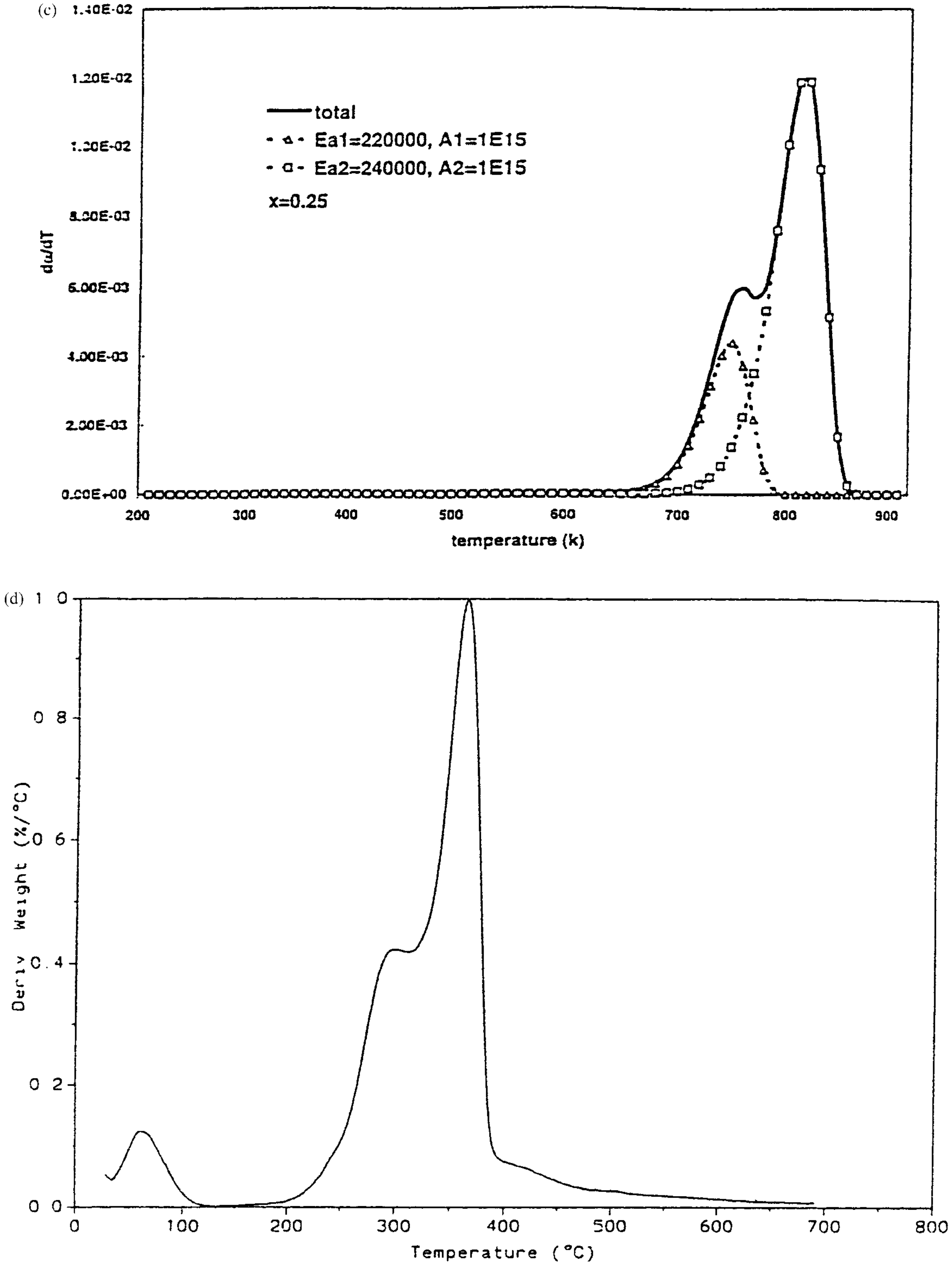


Fig. 3. (*Continued*)

The final DTG will then be determined by these two mechanisms, i.e.

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=x\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_1+(1-x)\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_2 \quad (8)$$

where subscript 1 denotes the first mechanism, subscript 2 the second mechanism and $x$ the weight assigned to each mechanism.

Fig. 3(a and c) show the simulated graphics of the two mechanisms, on which the value of $A$ and $E_a$ are shown on the plots, and (b) and (d) the corresponding experimental curves, i.e. DTG curve of spruce and red oak in nitrogen.

The similarity in the shape of the simulated and the experimental data shows that modeling of the thermal analysis results is an acceptable and reasonable one. However, where an overlapping of kinetic reaction sequence is suspected, it must be noted that the deconvolution of the DTG plot is not a unique solution as there are an infinite number of solutions to the curves shown in Figs. 1 and 2, based on the two kinetic reaction sequences, differ in order and the Arrhenius parameters. The earlier studies on cellulose [8,9] demonstrated that the rate-controlling mechanism was probably phase-boundary controlled. However, in sawdust, we have the additional complication of the presence of hemicellulose and lignin components as well as cellulose. These could contribute to the complexity of the process.

## 4. Conclusion

1. Thermal degradation behaviors of various wood species have been studied in the temperature range from 200° to 400°C, and their $A$ and $E_a$ values have been calculated by the derivative method.
2. The deviation of the theoretical from experimental data suggests that, in these complex natural cellulosic materials, at least two mechanisms coexist at some time, and contribute to the overlapping shown on the DTG curve, which is supported by the computer-simulated graphics.

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