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KINETICS OF THERMAL DECOMPOSITION OF CELLULOSE. PART I. INFLUENCE OF EXPERIMENTAL CONDITIONS

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ABSTRACT

The kinetics of weight loss in the thermal decomposition of cellulose have been determined by means of isothermal and dynamic experiments carried out under various conditions. Values for the pyrolyzable fraction, reaction order and kinetic constant have been obtained from isothermal experiments, while the important influence of the rate of heating of the system as well as the percentages of pyrolyzed solids at $T \leqslant 150\,^{\circ}\mathrm{C}$ have been observed from the dynamic experiments.

INTRODUCTION

The thermal decomposition of lignocellulosic materials takes place through a complex series of chemical reactions together with processes of mass and heat transfer [1]. This makes it extremely difficult to establish a clear mechanism for the pyrolysis.

In the literature [2–6] important differences may be observed in the results obtained on the kinetics of thermal decomposition of biomass. Although some authors state that these differences are due to the different materials used, this cannot be the only reason, as we can see when comparing the results reported for cellulose [2,4,7].

The reasons for these disagreements may include the following: (a) the use of different experimental equipments (e.g., thermobalance, fluidized bed), which can give rise to different types of pyrolysis, (b) the type of experiment (isothermal, dynamic), (c) the method used for data analysis, (d) the experimental conditions (temperature, heating rate, pressure), (e) the physical properties of the material (mainly, moisture content and particle size), (f) the chemical composition of the solid (contents of hemicellulose, cellulose, lignin and inorganic components).

The study tries to determine the influence of various experimental conditions when the thermal decomposition of the lignocellulosic material is studied from the kinetic point of view. This should help us to explain the different results found in the literature. Cellulose has been used throughout in order to eliminate the influence of the chemical composition of the material.

EXPERIMENTAL

Results for the weight loss of the material were obtained using a Perkin-Elmer TGS-2 thermobalance in a nitrogen atmosphere. Cellulose was supplied by Sigma Chemical Co.

In all the experiments the results have been expressed as a function of the conversion X, defined as

$$X = (W_0 - W)/W_0 \tag{1}$$

Prior to the kinetic study of cellulose pyrolysis, a series of experiments were made under various experimental conditions. This allowed us to identify and eliminate the influence of some of those conditions on the thermal decomposition of cellulose. From these experiments we obtained the following information. (i) The cellulose used "as received" was free from interparticle heat and mass transfer resistances. This was checked by grinding and decompacting cellulose, which gave very similar conversion vs. time results. (ii) For initial cellulose weights of less than 5 mg, the initial weight was found to exert no influence on the conversion obtained. (iii) Under a given set of experimental conditions, the conversion obtained at a given time was observed to be highly influenced by the fraction of the material weight lost *before* the beginning of the main decomposition (or "real" pyrolysis) of cellulose. Here, this fraction of the weight lost has been quantified as a variable H, defined as

$$H = 100(W_0 - W_1)/W_0 \tag{2}$$

where W_1 is the weight of the sample at $T = 150\,^\circ\mathrm{C}$.

An example of the influence of the H value is shown in Fig. 1. A decrease in the conversion obtained for the same pyrolysis time can be observed on increasing the H value. The higher the heating rate of the oven, the more remarkable this effect becomes; however it is not significant at low heating rates. This phenomenon may be explained by the different temperatures of the solid and of the oven, because the solid cools down owing to the intake of heat needed to lose the weight mentioned above.

For the kinetic study, and taking into account the relative rate of cellulose pyrolysis, dynamic experiments were carried out at various constant heating rates of the oven (80–1.25 °C min^{-1}).

In the same way, isothermal experiments were carried out in which the desired temperature was reached after preheating at a constant rate, in order

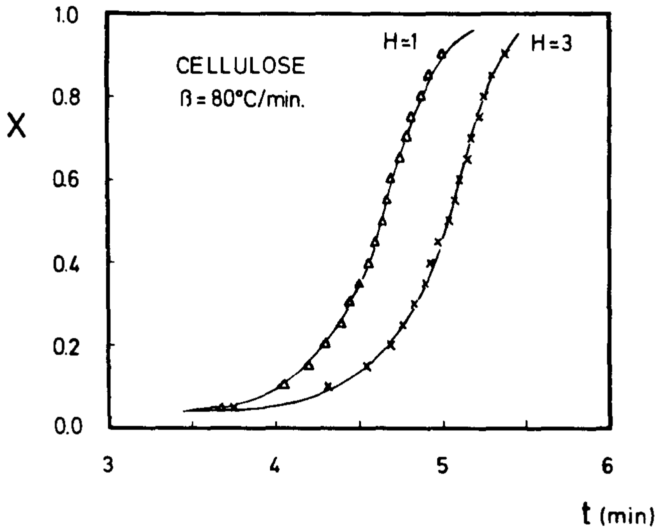

Fig. 1. Influence of *H* on the conversion.

to compare the different results since it appeared that there exist disagreements between them [7,8]. Values of the pyrolyzable fraction, *A*, defined as

$$A = (W_0 - W_\infty)/W_0 \tag{3}$$

were obtained for each temperature from these experiments; these values were needed for the data analysis used to determine the kinetic equation.

RESULTS UNDER ISOTHERMAL CONDITIONS

Isothermal experiments were carried out with a low preheating rate (1.25 °C min^{-1}) in order to avoid temperature differences between the system and the solid. The pyrolysis temperatures studied were in the range 230–300 °C. At lower temperatures only very small amounts of cellulose decomposed, while at temperatures higher than 300 °C nearly all of the solid had decomposed.

The values of the pyrolyzable fraction, *A*, were determined from the experiments at various temperatures and are shown in Fig. 2.

The reaction order was also determined from these experiments because different values for the kinetic order, ranging from 0 to 3, have been reported in the literature [9]. For a wide interval of weight, the mean kinetic order obtained is unity; the simplicity of such a relationship makes it suitable for use in engineering techniques. On the other hand, Lewellen et al. [10] obtained similar values when they compared a first-order simple equa-

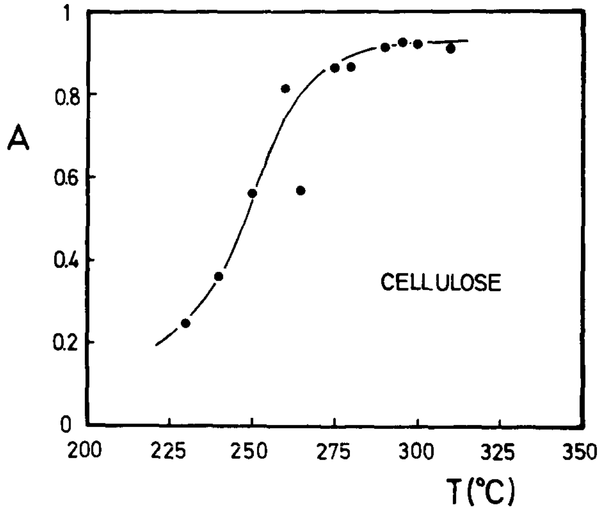

Fig. 2. Values of *A* for various temperatures.

tion with a multiple-reaction model based on a series of first-order, independent, parallel reactions.

In this work, we have used the equation

$$-\frac{1}{W_0}\frac{\mathrm{d}W}{\mathrm{d}t}=k\left(\frac{W-W_\infty}{W_0}\right)^n \tag{4}$$

Substituting eqns. (1) and (3) into eqn. (4), gives

$$\frac{\mathrm{d}X}{\mathrm{d}t}=k(A-X)^n \tag{5}$$

or

$$\log \mathrm{d}X/\mathrm{d}t=\log k+n\log(A-X) \tag{6}$$

Three different temperature intervals were considered: (a) low temperature (230–250 °C), where *A* varies greatly with temperature; (b) intermediate temperatures (260–280 °C), where only a slight variation in *A* can be observed; (c) high temperatures (> 290 °C), where the pyrolyzable fraction is close to unity. Each of these will now be examined in turn.

Low temperatures

At these temperatures (230–250 °C) a wide variation of *A* with temperature was observed. Therefore, in principle, the determination of *A* could be inaccurate. This could lead, in turn, to an error in the determination of *n* because, as will be shown, *n* depends upon the *A* value considered. The values of *n* can be obtained from the slope of the plot of log dX/dt vs.

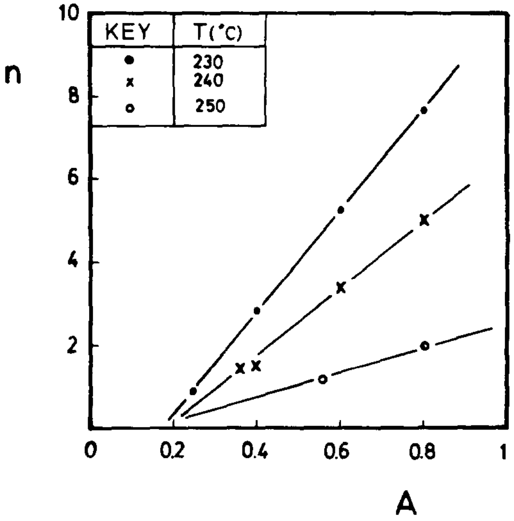

Fig. 3. Values of *n* corresponding to selected values of *A*.

log($A - X$) (eqn. 6) for various values of A. The lowest value of A used here corresponds to the one obtained experimentally in this study. Figure 3 shows the n values corresponding to each value of A. Although for the experimental values of A the reaction order is near unity, higher values of this reaction order may be observed if we increase A.

On the basis of the experimental values of A, eqn. (5) becomes

$$\frac{dX}{dt} = k(A - X) \tag{7}$$

which, upon integration with the initial conditions $t = t_i$; $X = X_i$, yields

$$\ln(A - X) = \ln(A - X_i) + kt_i - kt \tag{8}$$

The k values can be obtained from the slope of the plot of $\ln(A - X)$ vs. t and they are shown in Table 1. An unusual variation with temperature may be observed in the apparent kinetic constant. Since the dX/dt values increase with temperature, an increase in k would be expected as the temperature increases. However, this effect may be compensated by the fact

TABLE 1

A and *k* values for low temperatures

	T (°C)		
	230	240	250
A	0.246	0.361	0.561
k (min^{-1})	0.00137	0.00099	0.00164

that A also increases with temperature, thus giving rise to a decrease in the value of k. This variation of k with temperature may cause problems when the Arrhenius equation is employed, sometimes giving rise to negative values for the activation energy. This agrees with the objections of Brown [11] against the use of this equation to describe cellulose pyrolysis, although, as Baker [8] states, this equation is still very useful even though the theoretical meaning of the parameters in the Arrhenius equation cannot be extended to the decomposition of a solid.

From these data, it may be concluded that, when the pyrolyzable fraction A takes highly variable values, the same results for conversion vs. time may be fitted to different equations simply by modifying the value of A. For this reason, it is more appropriate to talk about equations fitted to the data obtained, rather than about "kinetic equations", although these equations are certainly useful from an engineering point of view because they allow the prediction of the conversion values as a function of time and temperature.

Intermediate temperatures

In the temperature range 260–280 °C, a plot of log dX/dt vs. $\log(A - X)$ for a given temperature, using the experimental value of A, gives rise to a change in the slope of the resulting line. However, for practical purposes, it may be assumed that for most of the reaction time the pyrolysis process exhibits first-order behaviour.

The kinetic constant has been determined using eqn. (8) and the experimental values of A; the results of this calculation are shown in Table 2.

Temperatures higher than 290 °C

From the plot of log dX/dt vs. $\log(A - X)$ a straight line with $n \approx 1$ is obtained for each temperature. The values of k obtained using eqn. (8) are shown in Table 2.

If a low preheating rate is used to obtain a high working temperature, by the time this temperature is reached most of the solid has already been pyrolyzed. For this reason isothermal experiments were carried out using a high preheating rate ($\beta = 80$ °C min^{-1}). The kinetic constants were determined using eqn. (8).

TABLE 2

A and k values for intermediate and high temperatures

	T (°C)					
	260	275	280	290	295	300
A	0.820	0.870	0.870	0.920	0.930	0.930
k (min^{-1})	0.0020	0.0110	0.0145	0.0300	0.0400	0.0510

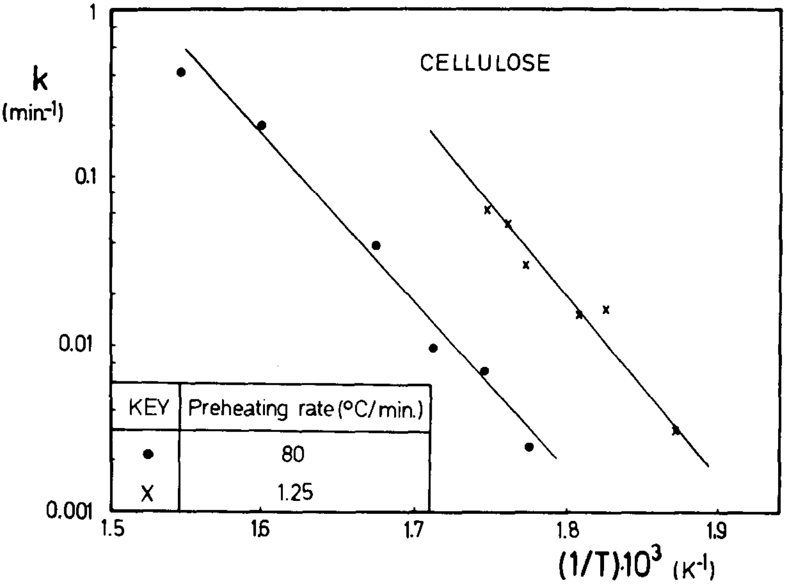

Fig. 4. Values of k obtained in isothermal experiments for various preheating rates.

Figure 4 shows the values of the kinetic constants obtained in isothermal experiments with preheating rates of 1.25 and 80 °C min^{-1}, respectively. It may be observed that the values obtained with a preheating rate of 1.25 °C min^{-1} are higher than those obtained at 80 °C min^{-1}. This is explained by the difference between the temperatures of the system and of the solid when the preheating rate is high. From these results, it may be concluded that, if the temperature of the solid is taken to be the same as the temperature of the system, the use of data obtained with high preheating rates can lead to significant errors.

RESULTS FROM DYNAMIC EXPERIMENTS

Results obtained from dynamic experiments (continuous heating) can be used to determine the kinetics of pyrolysis as temperatures higher than those at which the results obtained from isothermal experiments are valid. For this reason, experiments at various heating rates ranging from 1.25 to 80 °C min^{-1} have also been carried out.

The kinetic equation was taken to be first-order, and the value of the kinetic coefficient was obtained from eqn. (7) and the values of $\mathrm{d}X/\mathrm{d}t$ and $(A - X)$.

The results obtained in the different experiments were then compared. It can be seen that, for the same system temperature, the values of the apparent kinetic constants depend on the percentage pyrolyzed at $T \leqslant 150$ °C (H) and the heating rate in the system (β).

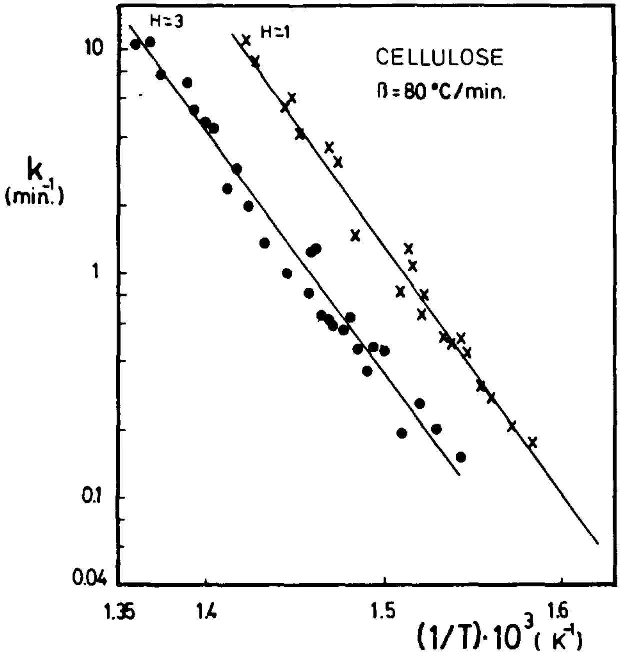

Fig. 5. Influence of *H* on the apparent kinetic constant with $\beta = 80\,°\mathrm{C}\ \mathrm{min}^{-1}$.

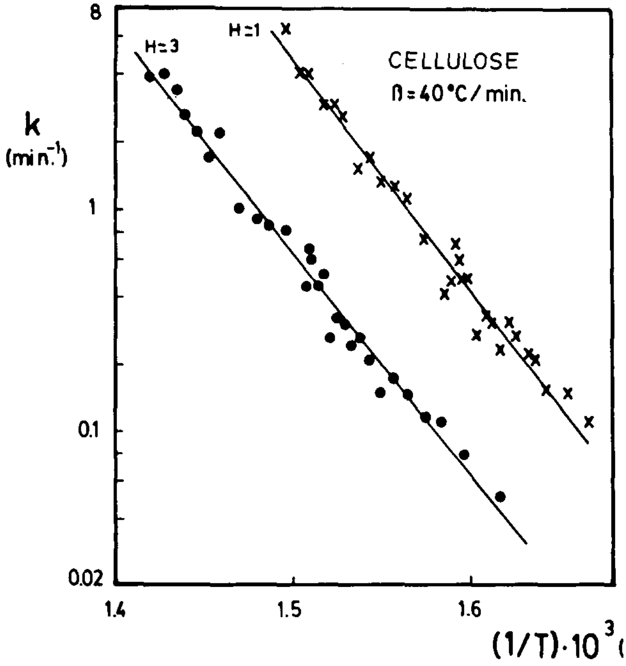

Fig. 6. Influence of *H* on the apparent kinetic constant with $\beta = 40\,°\mathrm{C}\ \mathrm{min}^{-}$

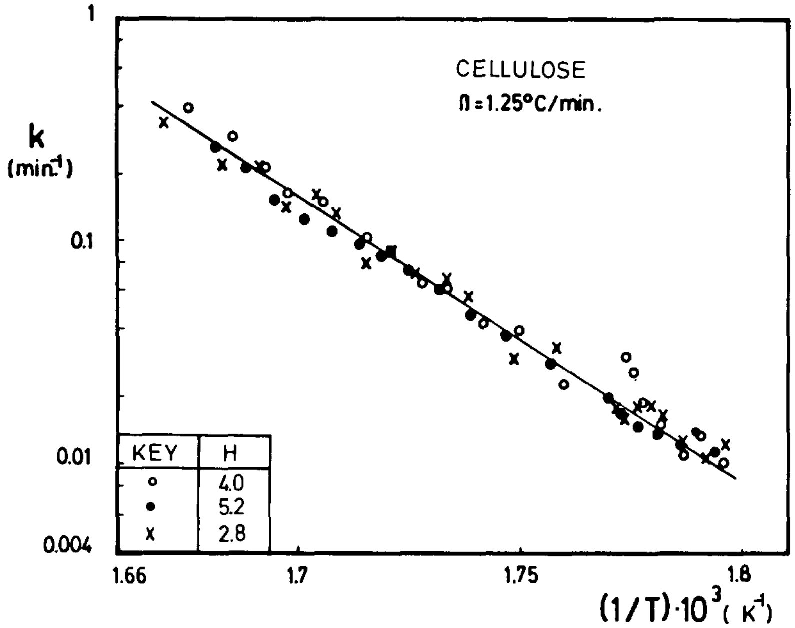

Fig. 7. Values of k obtained in dynamic experiments with $\beta = 1.25\,°\mathrm{C\ min^{-1}}$.

Some examples of the influence of H on the apparent kinetic constants are shown in Figs. 5 and 6. It can also be seen that, at the same heating rate and oven temperature, an increase in H leads to a decrease in k. This is thought to be due to a cooling of the solid caused by an endothermic process (mainly moisture evaporation) that gives rise to a temperature gap between the solid and the system. Some grounds for this hypothesis could be found if the effect of the H value were observed to be at a minimum at low heating rates. In Fig. 7, the values of k for $\beta = 1.25\,°\mathrm{C\ min^{-1}}$ and various values of H are shown: as can be seen, similar results were obtained for each temperature.

The values found for the apparent kinetic constant were compared in order to determine the influence of the heating rate. Because of the influence of the H value, the experiments were classified into groups having similar values of H: 2.3–2.9 in Fig. 8, and 1–1.5 in Fig. 9. Both figures show that, for a given temperature, an increase in the heating rate gives rise to a lower value of the kinetic constant. This is an unexpected result, since according to the proposed mechanism for biomass pyrolysis [12], an increase in the solid heating rate must lead to a higher conversion to volatile products. The decrease observed in the value of k could be explained in terms of a temperature gap between the solid and the system.

The observed effects of H and β make advisable the use of dynamic experiments at low heating rates to obtain the values of the kinetic constant.

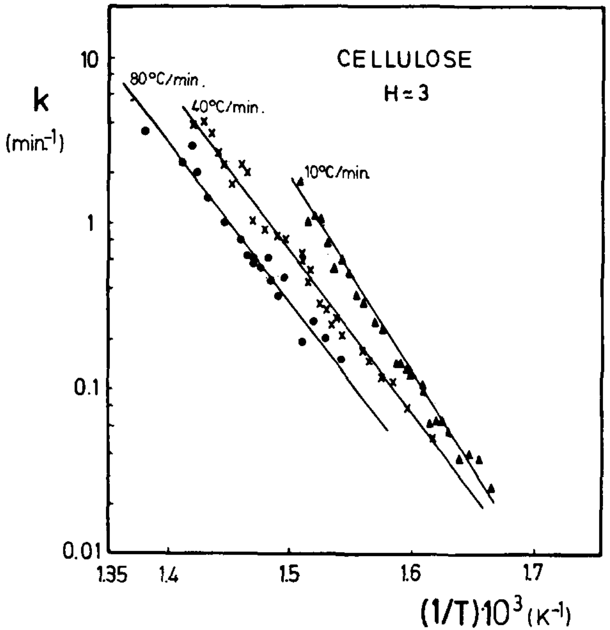

Fig. 8. Influence of the heating rate on the apparent kinetic constant.

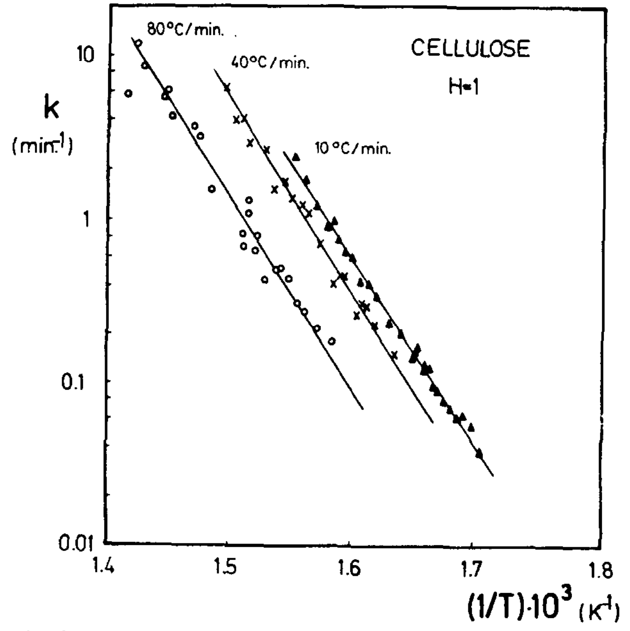

Fig. 9. Influence of the heating rate on the apparent kinetic constant.

Thus, from the dynamic experiments carried out at $\beta = 1.25\,^\circ\mathrm{C}\ \mathrm{min}^{-1}$ it was concluded that

$$k(\mathrm{min}^{-1}) = 3 \times 10^{19} \exp(-54300/RT) \qquad (9)$$

The use of a low heating rate presents one important difficulty: it is not possible to reach very high temperatures with significant amounts of solid. Equation (9) is valid for $T \leqslant 330\,^\circ\mathrm{C}$. To extend the scope of this equation to higher temperatures it is necessary to carry out the appropriate calculations in order to obtain the actual solid temperature for any given system temperature.

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REFERENCES

1 C.A. Zaror and D.L. Pyle, Proc. Indian Acad. Sci. (Eng. Sci.), 5 (4) (1982) 269.
2 A.F. Roberts, Combust. Flame, 14 (1970) 261.
3 C. Fairbridge and R.A. Ross, Wood Sci. Technol., 12 (1978) 169.
4 D.Q. Tran and Ch. Rai, Fuel, 57 (1978) 293.
5 H.A. Becker, A.M. Phillips and J. Keller, Combust. Flame, 58 (1984) 163.
6 M.J. Antal, H.L. Friedman and F.E. Rogers, Combust. Sci. Technol., 21 (1980) 141.
7 R.D. Cardwell and P. Luner, Wood Sci. Technol., 10 (1976) 131.
8 R.R. Baker, Thermochim. Acta, 23 (1978) 201.
9 R.R. Baker, J. Thermal Anal., 8 (1975) 163.
10 P.C. Lewellen, W.A. Peters and J.B. Howard, paper presented at 16th Symp. Int. on Combustion, Pittsburgh, PA, 1977, p. 1471.
11 D.J. Brown, Thermochim. Acta, 54 (1982) 377.
12 R.G. Graham, L.K. Mok, M.A. Bergougnou and H.I. De Lasa, paper presented at 4th Bioenergy R.&D. Seminar, Winnipeg, Manitoba, 1982, p. 29.