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## **PYROLYSIS KINETICS OF WOOD COMPARISON OF ISO- AND POLYTHERMAL THERMOGRAVIMETRIC METHODS**

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### **ABSTRACT**

The values of kinetic parameters  $E_a$  (activation energy) and A (preexponential factor) were evaluated for different kinetic models using data from thermogravimetric (TGA) curves obtained in isothermal and polythermal conditions. It was found that diffuse kinetic models D3 and D4 approximated the experimental data better than first order reaction model F1. The values of kinetic parameters for D3 and D4 models evaluated from both types of TG curves were comparable.

**Key words:** kinetics of pyrolysis, kinetic models, thermogravimetric analysis.

### **INTRODUCTION**

Wood thermal decomposition is considered a promising process of efficient and, in future, economically profitable conversion of this raw material into high quality energetic and chemical products. However, designing technologies based on the pyrolysis of renewable lignocellulosic raw materials requires good knowledge of the kinetics of this process.

The thermal dissociation of a solid is a very complex process which occurs in a hetero-phase system in which several stages can be distinguished which are associated both with heat transport as well as a discharge of vapour-gas products of decomposition or development of a new solid phase. The obtained result of the performed experiment showing the correlation between the degree of conversion (L) and time (t) constitutes a sum result of all physical phenomena and chemical reactions as affected, to varying degrees, by both sample properties and measurements conditions.

Investigations on the kinetics of the process of thermal decomposition carried out using of thermogravimetric methods (TGA) can be carried out either in quasi-isothermal or polythermal conditions. It is not very difficult to prove the superiority of one of the methods over the other, because the functional dependence between the reaction rate constant (k) and temperature (T) and time is determined more accurately in isothermal conditions [4, 13] and, therefore, majority of research on the thermal kinetics of decomposition of lignocellulosic raw materials is based on this type of measurements [2, 3, 6, 8, 11, 12, 18]. Nevertheless, some of the published results are based on polythermal measurements [9, 10, 16, 18], which allow calculating kinetic parameters on the basis of one TGA curve. Therefore, it appears expedient to compare kinetic parameters of the thermal decomposition of samples derived from identical raw material calculated on the basis of both measurement methods with the aim to demonstrate whether the F1 kinetic model most commonly adopted for the pyrolysis process of lignocellulosic materials best describes experimental data.

In isothermal investigations, the non-isothermal stage of sample heating to the measurement temperature is unavoidable and, hence, the suggestion to apply a more accurate term for these methods, i.e. quasi-isothermal. The range of temperatures in which investigations are carried out is limited, on the one hand, by the temperature at which the process is initiated and, on the other, by the requirement to maintain a constant temperature during rapid changes occurring in the sample. When carrying out measurements within the limits of this range of temperatures, we obtain a series of isothermal kinetic curves, which cover the area of the diagram illustrating the dependence of L on t.

The rate of the examined reaction (process) is expressed by the following equation:

$$dL/dt = k(T)f(L) \quad (1)$$

in which:

k(T) – rate constant dependant on temperature,

f(L) – function describing the degree of progress of the reaction.

The range of the reaction expressed by the degree of progress of the reaction is calculated as follows:

$$L = (c_0 - c_t)/(c_0 - c_\infty) = (n_0 - n_t)/(n_0 - n_\infty) = (m_0 - m_t)/(m_0 - m_\infty) \quad (2)$$

where:

c<sub>0</sub> – initial concentration,

n<sub>0</sub> – initial number of moles,

m<sub>0</sub> – initial weight of the reagent,

c<sub>t</sub>, n<sub>t</sub>, m<sub>t</sub> – appropriate values after time t,

c<sub>∞</sub>, n<sub>∞</sub>, m<sub>∞</sub> – equilibrium values (terminal) of concentration, mole number or weight.

The basic equation of the reaction kinetics suggested by Arrhenius adopts the following form:

$$k = A \exp (-E_a /RT) \quad (3)$$

where:

k – rate constant,

A – frequency factor,

E<sub>a</sub> – activation energy,

R – gas constant,

T – temperature.

After the integration of equation (1) and the introduction of the designation:

$$\int_0^L dL/f(L) = g(L)$$

corresponding to the total form f(α), we obtain:

$$g(L) = kt \quad (4)$$

In order to describe the process of thermal decomposition, several equations derived from three basic functions characterising the stage limiting the total rate of the process are applied:

- development of centres of new solid phase,
- reactions at the boundary of substrate-product phase,
- diffusion of gaseous reaction products.

Sestak and Berggren [15] suggested a generalisation of the equation for the rate of the reaction:

$$dL/dt = k(1 - L)^n L^m - \ln(1 - L)^p \quad (5)$$

Pysiak and Pacewska (1996) correlated kinetic equations in integral g(L) and differential f(L) forms depending on exponential values of the Sestak-Berggren equation (Table 1).

**Table 1. The integral [g(L)] and differential [f(L)] form of kinetic equations used to describe solid dissociation process and exponents of Sestak- Berggren equation [14]**

Model's symbol	Integral form g(L)	Differential form f(L)	Exponents of Sestak-Berggren equation [15]		
			m	n	p
R1	L	(1-L) <sup>0</sup>	0	0	0
D1	L <sup>2</sup>	(1/2)L <sup>-1</sup>	-1	0	0
P3	L <sup>1/2</sup>	2L <sup>1/2</sup>	1/2	0	0
P2	L <sup>1/3</sup>	(3/2)L <sup>2/3</sup>	2/3	0	0
P1	L <sup>1/4</sup>	(4/3)L <sup>3/4</sup>	3/4	0	0
R2	1-(1-L) <sup>1/2</sup>	2(1-L) <sup>1/2</sup>	0	1/2	0
R3	1-(1-L) <sup>1/3</sup>	3(1-L) <sup>2/3</sup>	0	2/3	0
F1	-ln(1-L)	(1-L)	0	1	0
(A)	[-ln(1-L)] <sup>2/3</sup>	3/2(1-L)[-ln(1-L)] <sup>1/3</sup>	0	1	1/3
A2	[-ln(1-L)] <sup>1/2</sup>	2(1-L)[-ln(1-L)] <sup>1/2</sup>	0	1	1/2
A3	[-ln(1-L)] <sup>1/3</sup>	3(1-L)[-ln(1-L)] <sup>2/3</sup>	0	1	2/3
A4	[-ln(1-L)] <sup>1/4</sup>	4(1-L)[-ln(1-L)] <sup>3/4</sup>	0	1	3/4
D2	L + (1-L)ln(1-L)	[-ln(1-L)] <sup>-1</sup>	0	1	-1
D4	1 - 2L/3 - (1-L) <sup>2/3</sup>	(3/2)[(1-L) <sup>-1/3</sup> - 1] <sup>-1</sup>			
D3	[1 - (1-L) <sup>1/3</sup> ] <sup>2</sup>	3(1-L) <sup>2/3</sup> [1 - (1-L) <sup>1/3</sup> ] <sup>-1</sup>			
F2	(1-L) <sup>-1</sup> - 1	(1-L) <sup>2</sup>	0	2	0

The correlation of L and t obtained in the discussed experiment is a function of three kinetic parameters, namely: A and E<sub>a</sub> from the Arrhenius equation and a form of g(L) function which, theoretically, depended on the reaction mechanism. The choice of this function was important because of the need to match, as best as possible, correlations resulting from it to experimental results and its possible correlation with process mechanisms.

Polythermal methods are frequently applied in investigations on the kinetics of thermal decomposition because they allow determining E<sub>a</sub> values from one curve describing the dependence of the degree of conversion on time and/or temperature. In conditions of a polythermal analysis, TG curves portray Δm = f(T) relationships, hence also L = f(T) and it is temperature and not time that constitutes a parameter.

The cases that are considered most frequently refer to analyses with a linear temperature increase whose rate equals:

$$V = dT/dt \quad (6)$$

When correlation (3) resulting from (5) is substituted into equation (1), the following differential equation is obtained:

$$dL/dT = (A/V) f(L) \exp[-E_a / (RT)] \quad (7)$$

When, in turn, equation (6) is integrated, it leads to:

$$t = T/V \quad (8)$$

and, after substituting into equation (4) and taking into consideration (3), it results in:

$$g(L) = (AT/V)\exp[-E_a/(RT)] \quad (9)$$

The procedure of  $g(L)$  function selection in the course of isothermal measurements involves the choice of such of its form for which it will be possible to obtain, at constant temperature, a linear relationship to time. In such situation,  $k(T)$  is a directional coefficient and when it is determined at different temperatures,  $E_a$  and  $A$  can be calculated from the logarithmic form of equation (3):

$$\ln k(T) = \ln A - (E_a/R)(1/T) \quad (10)$$

which describes the linear dependence of  $\ln k$  on  $1/T$ .

In the case of non- isothermal TGA curves, the function which approximates these data assumes the following form:

$$\ln[g(L)/T] = \ln(A/V) - (E_a/R)(1/T) \quad (11)$$

Therefore, such a form of  $g(L)$  function is sought at which the left side of the equation is the linear function of temperature inversion allowing to determine  $E_a$  and  $A$  parameters.

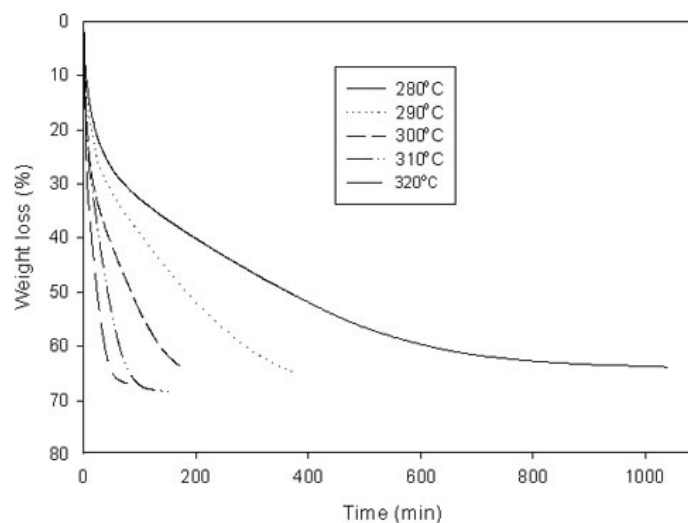
The goal of this study was to determine a kinetic model which best fitted the TGA curves describing the thermal degradation process of the investigated kinds of wood under iso- and polythermal conditions.

### EKSPERIMENTAL

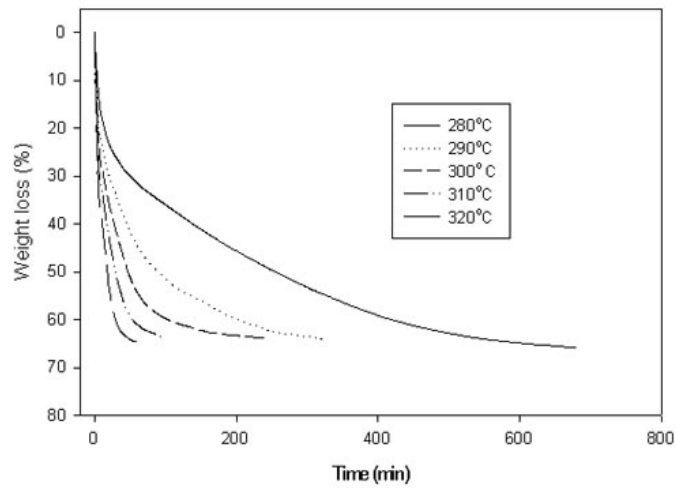
Investigations were carried out on wood samples derived from beech and pine. Samples were prepared from wood which was air conditioned at the temperature of  $20 \pm 2^\circ\text{C}$  and kept at the relative humidity (RH) of  $60 \pm 5\%$ . The wood material was comminuted to particles ranging from 0.5 to 1.5 mm following the suggestion made by Bilbao et al. [5] who maintain that this allows minimising the effect of heat conduction on the course of thermal decomposition.

Investigations, which allowed determining the correlation of sample weight losses in time or temperature function, were carried out on a Setaram Company Labsys TM thermobalance using weighed portions of 20 mg weight. Sample weight losses, which were the measure of the reaction progress, were recorded on TGA curves during iso- and polythermal measurements. Experiments in quasi-isothermal conditions were carried out in the temperature range of  $265\text{--}350^\circ\text{C}$  (Fig.1 and 2). In polythermic investigations, the heating rate was 5 deg/min, and the final measurement temperature was established at the level of  $600^\circ\text{C}$  (Fig.3 and 4). All the analyses were carried out in the atmosphere of flowing helium with the sample placed in an open platinum crucible.

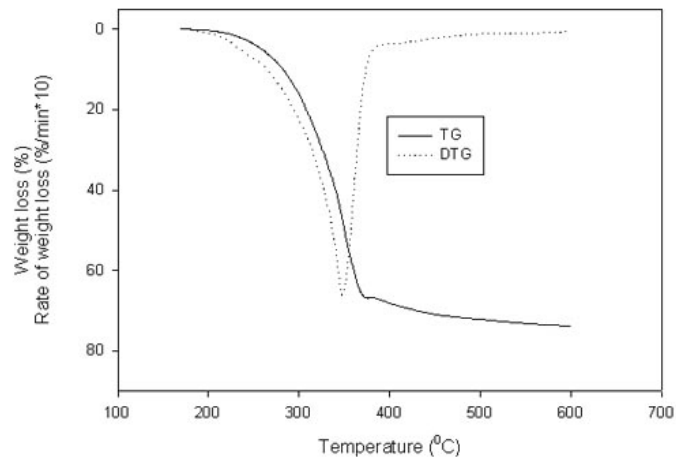
**Fig. 1. TG curves run during quasi-isothermal degradation of pine wood**



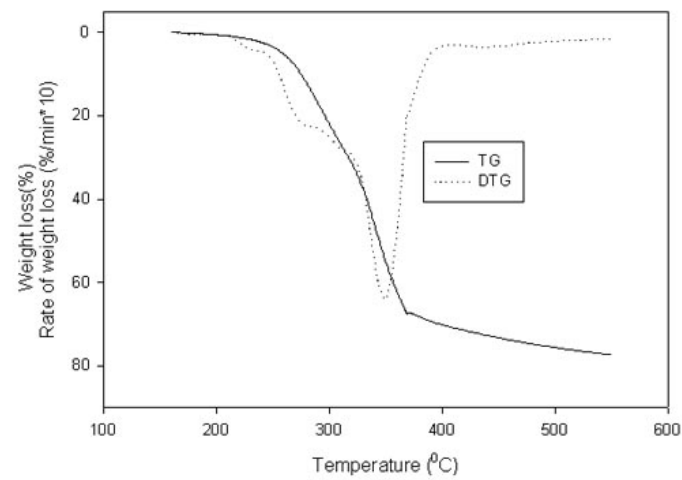
**Fig. 2. TG curves run during quasi-isothermal degradation of beech wood**



**Fig. 3. TG and DTG curves run during thermal degradation of pine wood (V= 5 deg/min; atmosphere- helium)**



**Fig. 4. TG and DTG curves run during thermal degradation of beech wood (V= 5 deg/min; atmosphere- helium)**



In isothermal investigations, at least four measurements were taken for each raw material for weight losses in time function in temperatures, which were included in the above-mentioned interval. The obtained TGA curves were subjected to statistical-mathematical analysis with the aim to determine the kinetic model, which would best describe the process of thermal decomposition of the examined materials. When selecting function  $g(L)$ , the following criteria were adopted:

- correlation coefficient  $r^2$ ,
- criterion S

$$S = \sum_{j=1}^n (L_{d,j} - L_{o,j})^2 \quad (12)$$

in which:

$n$  – number of values of the degree of conversion in a given temperature,

$L_{d,j}$ – degree of conversion determined experimentally,

$L_{o,j}$ – degree of conversion calculated from Arrhenius equation.

The S criterion was calculated in such a way that, in at least four temperatures, constant rates  $k$  were determined for individual kinetic models. Next, A and  $E_a$  parameters were calculated for  $g(L)$  function forms corresponding to them using the logarithmic form of equation (3) and from them –  $L_o$  values. For all pairs of  $L_{d,j}$  and  $L_{o,j}$  values, the value of the S criterion was determined for each temperature in accordance with equation (12), followed by  $\sum S$  within the examined model.

The function which best described a given experiment should have the value of the first criterion as close to 1 as possible and the smallest value of the second criterion.

In polythermal investigations, values of kinetic parameters were calculated for the rate of temperature rise of 5 deg/min, while criteria selection for the kinetic model were as follow: their numerical values (appropriately comparable with those calculated for isothermal measurements) as well as correlation coefficients calculated during the linearisation of equation (11).

The results shows in [Table 2](#) and [3](#).

**Table 2. Kinetic parameters: activation energy ( $E_a$ ) and preexponential factor (A) and criteria:  $r^2$  and S of thermal degradation process of pine wood calculated from iso- and polythermal TG curves**

Kinetic model	Isothermal				Polythermal		
	$E_a$	A	$r^2$	S	$E_a$	A	$r^2$
F1	190.8	$3.5 \times 10^{15}$	0.9870	0.8747	91.8	$6.4 \times 10^5$	0.9876
R3	185.6	$2.9 \times 10^{14}$	0.9657	1.4397	85.6	$4.9 \times 10^4$	0.9938
D1	184.9	$3.7 \times 10^{14}$	0.9758	0.4197	156.7	$7.0 \times 10^{10}$	0.9896
D2	189.4	$7.3 \times 10^{14}$	0.9930	0.1321	164.7	$2.4 \times 10^{11}$	0.9939
D3	197.8	$1.6 \times 10^{14}$	0.9844	0.1865	175.8	$7.1 \times 10^{11}$	0.9942
D4	191.8	$3.3 \times 10^{14}$	0.9929	0.1019	168.3	$1.2 \times 10^{11}$	0.9946

**Table 3. Kinetic parameters: activation energy ( $E_a$ ) and preexponential factor (A) and criteria:  $r^2$  and S of thermal degradation process of beech wood calculated from iso- and polythermal TG curves**

Kinetic model	Isothermal				Polythermal		
	$E_a$	A	$r^2$	S	$E_a$	A	$r^2$
F1	182.4	$7.8 \times 10^{14}$	0.9818	1.0938	97.0	$9.3 \times 10^5$	0.9906
R3	180.8	$1.4 \times 10^{14}$	0.9477	1.9425	89.8	$5.5 \times 10^4$	0.9899
D1	180.6	$1.9 \times 10^{14}$	0.9509	0.6023	162.3	$2.1 \times 10^{11}$	0.9793
D2	182.1	$2.1 \times 10^{14}$	0.9816	0.1720	171.4	$9.5 \times 10^{11}$	0.9830
D3	184.6	$1.4 \times 10^{14}$	0.9900	0.0968	184.1	$4.4 \times 10^{12}$	0.9905
D4	182.9	$6.7 \times 10^{13}$	0.9888	0.0933	175.5	$5.6 \times 10^{11}$	0.9862

## DISCUSSION OF RESULTS

It is evident from earlier considerations [17] that kinetic models referring to processes of formation of development centres of a new phase (models of A and P type) as well as R1, R2 and F2 models are not very useful because of values of correlation coefficients corresponding to them which were smaller than 0.95. That is why the present study was confined to the consideration of the following models: R3 – volume shrinkage, F1 – kinetics of the first order reactions as well as “diffuse” models D1-D4.

Curve courses of sample weight losses in time determined at different temperatures were used to determine the dependence of  $\alpha$  on  $t$  at the assumption that  $m_\infty$  corresponded to 70% of the initial sample weight loss. Calculations were performed in accordance with the procedure described in the case of isothermal measurements.

Numerical data from the temperature interval of 180-360°C, which was delineated by the area  $0 \leq \alpha \leq 1$ , were adopted to determine kinetic parameters from polythermal TGA curves.

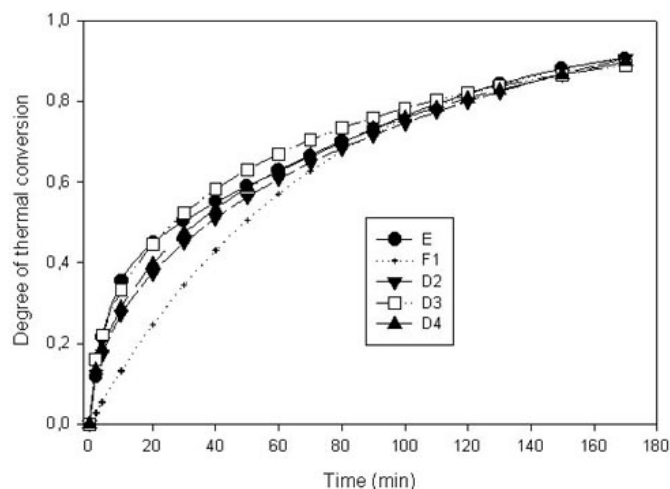
Numerical values of  $E_a$  and A parameters calculated on the basis of isothermal analyses are similar to the considered kinetic models and are contained within appropriate intervals: 180.6-197.8 kJ/mol and  $6.7 \cdot 10^{13} - 3.4 \cdot 10^{15} \text{ min}^{-1}$ . On the basis of the adopted criteria, D3 and D4 models were found to be models which best described experimental data. The same models can be indicated as appropriate when calculating kinetic parameters on the basis of data from TGA curves determined in dynamic conditions. For these models, calculated values  $E_a$  and A are comparable with the appropriate values for isothermal measurements, while the respective correlation coefficients are within the  $0.990 \pm 0.005$  interval.

In the case of the F1 model, i.e. the one which is applied most frequently in considerations of the kinetics of the thermal decomposition process of wood and its constituents,  $E_a$  values calculated for polythermal measurements were by 50% smaller in comparison with the corresponding values which were calculated on the basis of isothermal data with correlation coefficients similar to those which were characteristic for D3 and D4 models. Results of  $E_a$  and A calculations for model R3 are comparable with model F1.

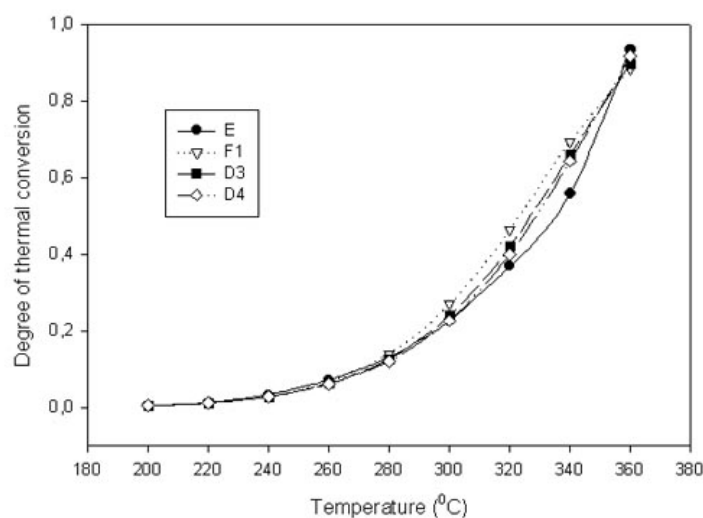
It was also observed that values of frequency factors were found to increase with the increase in the value of the activation energy, which confirms the existence of the compensatory effect described by Agrawal [1].

Considerable differences in values of kinetic parameters calculated on the basis of isothermal and polythermal analyses assuming the reaction kinetics of the first degree (model F1) may encourage a more critical approach towards the application of non-isothermal methods in investigations dealing with the kinetics of the thermal decomposition process of lignocellulosic materials.

**Fig. 5. Comparison of experimental (E) and theoretical curves evaluated from  $E_a$  and A for different kinetic model describing relationship of  $L$  vs.  $t$  during isothermal degradation of pine wood at 300°C**



**Fig. 6. Comparison of experimental (E) and theoretical curves evaluated from Ea and A for different kinetic model describing relationship of L vs. T during polythermal degradation of pine wood**



The expansion of considerations to cover other kinetic models allows indicating that models D3 and D4 are much better matched to experimental data. Also the comparison of courses of experimental and theoretical curves determined on the basis of appropriate kinetic parameters (Fig. 5 and 6) leads to a similar conclusion. These runs, in the case of D3 and D4 models, are closer to the experimental curve in comparison with the F1 model and this refers both to data from isothermal and polythermal measurements. This was also found by Zakrzewski [17] not only for wood but also for other lignocellulosic materials. The application of these models allowed obtaining comparable values of kinetic parameters of wood thermal decomposition on the basis of both iso- and polythermal methods. It should be emphasised that it is essential to be very careful to read any physical sense into these parameters and draw conclusions regarding the reaction mechanism bearing in mind convincing arguments given by Garn [7] who is very critical with regard to the utilisation of the theory of the active complex to describe changes in a solid.

## CONCLUSIONS

1. The D3 and D4 models from the group of diffuse kinetic models were found to best describe the TGA curves run obtained during thermal degradation of wood under iso- and polythermal conditions.
2. The application of the S criterion objectivized the selection of kinetic model.
3. The fact that models best fitting the experimental data were diffuse models did not necessarily indicate that the rate of wood thermal degradation was limited by diffusion mechanism.

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