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## **THE KINETICS OF THE THERMAL DECOMPOSITION OF THE WILLOW WOOD (*SALIX VIMINALIS* L.) EXPOSED TO THE TORREFACTION PROCESS**

*The aim of the study was to analyze the kinetic parameters (activation energy  $E_a$ , pre-exponential coefficient  $A$ , rate constant  $k$ ) of thermolysis in torrefied and raw willow wood (*Salix viminalis* L.), as well as to determine the effect of thermal modification conditions on the kinetics of this process. Samples of raw and torrefied willow wood in a steam atmosphere were analysed. The samples were subjected to thermogravimetric analysis under isothermal conditions. Analyses were conducted in an atmosphere of helium at 270–330°C. TG and DTG curves were recorded. The thermal characteristics of the samples were based on thermogravimetric analysis under dynamic conditions at a temperature of up to 600°C. On the basis of the data obtained from the TGA analyses, the kinetic parameters were calculated and statistical and mathematical analyses of the results were performed.*

**Keywords:** thermal analysis, thermal decomposition, pyrolysis, kinetic, torrefaction process, torrefied willow wood.

### **Introduction**

The energy supply system worldwide is based mainly on fossil fuels. Fuels such as coal, oil or natural gas at present cover 80% of total energy demand. Estimated resources of these fuels at current extraction trends may be depleted within the next 100 years, thus in recent years research on renewable energy sources has been greatly intensified. According to estimates, global resources of renewable energy considerably exceed the resources of traditional energy carriers [Konieczny 2005]. Increased interest in renewable energy sources is also due to ecological concerns.

The primary cause of greenhouse gas concentration in the atmosphere is related to carbon dioxide emissions coming from the combustion of fossil fuels. In the

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opinion of numerous researchers, if emissions of noxious gases are not reduced by 70% by the middle of the 21st century in order to recreate the Earth's protective shield, mankind will be affected by environmental changes on a much larger scale than previously experienced [Grzybek 2005].

One method to reduce carbon dioxide emissions into the atmosphere is to replace conventional energy sources with their ecological alternatives. In recent years the most dynamic development has been observed in the utilization of biomass as a renewable energy source. Biomass comprises many plant raw materials. Among them we may distinguish wood, agricultural raw materials, non-woody raw materials and industrial waste (e.g. from the pulp and paper industry) as well as municipal waste, represented for example by cellulose materials. Lignocellulosic materials predominate among biomass raw materials. They include wood materials and components of non-woody raw materials, e.g. fruit stones and shells, straw, etc.

Even at present biomass has great potential for utilization, since it is produced annually in amounts equivalent to ten times the heat energy demand worldwide [Grzybek 2005]. Its only drawback stems from the fact that, as in the case of other renewable energy sources, it is scattered and unevenly distributed on a global scale. A problem with the utilization of biomass as a source of energy may also result from the lack of a standard classification system comparable for instance to the ASTM classification system for coal. We do not know whether the course of thermal decomposition of a cob of maize, for example, is similar to the pyrolysis of wood. This requires a fundamental understanding of this process. Insight into the mechanism of pyrolysis, particularly the kinetics of this process, is essential for the understanding and prediction of the pyrolysis behavior of individual combined biomass components.

Studies on pyrolysis processes in lignocellulosic materials have been conducted using many different techniques, e.g. thermogravimetric analysis (TGA), differential thermal analysis (DTA) [Ramiah 1970; Fairbridge, Ross, Spooner 1975] and differential scanning calorimetry (DSC) [Zakrzewski 2001; MüllerHagedorn et al. 2003].

Some components and properties of biomass may be modified, making it possible to utilize as renewable fuel. This may be facilitated by biomass torrefaction [Bergman, Kiel 2005; Felfi et al. 2005; Lipinsky, Arcate, Reed 2002]. Torrefied wood is not a new product. Already in 1980 the French industry tried to use torrefied wood as a substitute for charcoal [Arcate 2002].

The aim of this study was to determine the kinetic parameters (activation energy  $E_a$ , pre-exponential coefficient  $A$ , rate constant  $k$ ) of thermolysis for torrefied and raw willow wood and to determine the effect of thermal modification conditions on the kinetics of this process. Calculations were made based on data obtained from thermogravimetric analysis under isothermal conditions.

## Materials and methods

Analyses were conducted on 0.5–1.0 mm fractions of sawdust from raw and torrefied willow wood (*Salix viminalis* L.). The torrefaction process was run at the Institute of Chemical Wood Technology under the following conditions:

- process temperature 200°C, duration of the process 6 h, steam application time 6 h (W-200-6-H<sub>2</sub>O),
- process temperature 200°C, duration of the process 12 h, steam application time 6 h (W-200-12-H<sub>2</sub>O),
- process temperature 200°C, duration of the process 24 h, steam application time 6 h (W-200-24-H<sub>2</sub>O).

Research on the thermal decomposition of the raw and the torrefied willow wood were conducted on a Labsys™ Setaram TG-DTA/DSC thermobalance. Thermal analysis, constituting the basis for studies on the kinetics of thermolysis in raw and torrefied willow wood, was conducted under isothermal (quasi-isothermal) conditions. Thermogravimetric analyses were run in an atmosphere of helium at a temperature of 270°C, 285°C, 300°C and 330°C while the temperature of decomposition was obtained at a dynamic increase in temperature. The mass of the samples tested was 20.0 ± 1.0 mg. During the analyses, TG and DTG curves were recorded.

The thermal characteristic of the analysed material was based on the thermogravimetric analysis under dynamic conditions. The established final temperature of the measurements was 600°C. Analyses were run in the atmosphere of an inert gas (helium). TG and DTG curves were recorded.

### Kinetics of the thermal decomposition

The principal equation of the reaction kinetics is the Arrhenius equation. It presents a dependence between the reaction rate constant  $k$  and the temperature:

$$k = A \exp - \left( \frac{E_a}{RT} \right) \quad (1)$$

where:  $k$  – reaction rate constant,

$A$  – pre-exponential coefficient [min<sup>-1</sup>] lub [s<sup>-1</sup>],

$E_a$  – activation energy [J/mol] lub [cal/mol],

$R$  – gas constant,

$T$  – temperature [K].

The reaction rate of the thermal dissociation of solids is described using two independent functions: rate constant  $k$  whose dependence on the temperature is presented by the Arrhenius equation, and the function dependent on the degree of transformation ( $\alpha$ ) designated as  $f(\alpha)$ :

$$\frac{d\alpha}{dt} = k f(\alpha) \quad (2)$$

The degree of transformation ( $\alpha$ ) is calculated as follows:

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_\infty)} \quad (3)$$

where:  $m_0$  – initial mass of the reagent,  
 $m_t$  – appropriate values after time  $t$ ,  
 $m_\infty$  – final mass.

The mathematical model of the function  $f(\alpha)$  is presented in the integral form designated as  $g(\alpha)$ :

$$g(\alpha) = k t \quad (4)$$

where:  $t$  – time,  
 $k$  – rate constant from Arrhenius equation.

It can be seen from the above equations that a dependence between the degree of the  $\alpha$  conversion and time, in other words – the experimentally-determined research results, is a function of three kinetic parameters: the pre-exponential coefficient  $A$ , activation energy  $E_a$  and the form of expression  $g(\alpha)$ .

Knowledge of the function  $f(\alpha)$  or its integral form  $g(\alpha)$  is necessary for the interpretation of the experimental results of the experiments. The problem of selecting function  $g(\alpha)$  is significant for two reasons. One is connected with the best possible fit of experimental results to the assumed theoretical model. The other reason is linking the function with the mechanism of the reaction, which enables the drawing of conclusions about the process course on the basis of kinetic data [Kielczewski, Zakrzewski, Bartkowiak 2003].

For each experimental material the mass loss was measured as a function of time at four different temperatures: 270, 285, 300 and 330°C. Plotted TG curves were subjected to statistical and mathematical analysis. In order to establish the function  $g(\alpha)$ , which best described the process of pyrolysis, three kinetic models were selected:

- F1:  $-\ln(1-\alpha)$  – growth of individual radical (first order kinetic process),
- D3:  $(1-(1-\alpha)^{1/3})^2$  – three-dimensional diffusion,
- R3:  $1-(1-\alpha)^{1/3}$  – three-dimensional translocation (volume shrinkage).

The following criteria were applied in order to select of function  $g(\alpha)$ :

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

$$S = \sum (\alpha_d - \alpha_o)^2 \quad (5)$$

where:  $\alpha_d$  – experimentally-determined degree of transformation,  
 $\alpha_o$  – degree of transformation determined from the Arrhenius equation.

Numerical values  $\alpha_d$  were calculated for individual temperatures and for the analysed models, also  $g(\alpha)$  values. Linearizing the dependence  $g(\alpha)$  of  $t$  for each temperature, constant speed  $k$  and correlation coefficients  $r^2$  of the linearization were determined. In turn, from the logarithmic form of the Arrhenius equation (1):

$$\ln k_d = \ln A - \left( \frac{E_a}{R} \right) \left( \frac{1}{T_d} \right) \quad (6)$$

coefficients  $A$  and  $E_a$  were calculated using linear regression. These coefficients were used to calculate values of  $\alpha_o$ , solving the equation (4):

$$g(\alpha) = k_d t \quad (7)$$

For all pairs  $\alpha_d$  and  $\alpha_o$  the value of criterion  $S$  for each temperature, and then  $\Sigma S$  within the investigated kinetic model were calculated.

Among the selected kinetic models, function  $g(\alpha)$ , which has the value of the first criterion (correlation coefficient) closest to 1, and the value of criterion  $S$  the smallest possible, is the function best describing the experimental data.

## Results and discussion

### The thermal characteristic of raw and torrefied willow wood

Table 1 presents the thermal characteristic of the tested material. The process of the thermal decomposition of raw and torrefied willow wood takes place within one temperature range of active thermolysis. The field of increased dynamics of pyrolysis in raw wood covers the range of temperatures from 204°C to 362°C. In the case of the willow wood subjected to 6 h hydrothermal treatment (W-200-6-H<sub>2</sub>O), the beginning of the increase in thermolysis dynamics was recorded at a temperature of 207°C, while for the wood modified for 12 and 24 h (W-200-12-H<sub>2</sub>O, W-200-24-H<sub>2</sub>O), it was at 210°C. The intensity of the thermal decomposition of torrefied willow wood decreases after the temperature of 360°C is exceeded.

In the areas of the active thermolysis of the experimental material, two temperatures each were established for the maximum decomposition rate (table 1). One, contained within the range of 260–269°C, may be related to the pyrolysis of the carbohydrate compounds of the lignocellulosic materials, while the other, covering the range of 333–334°C, to the thermolysis of the aromatic compounds of the raw material [Prosiński 1984; Fengel, Wegener 1989].

Moreover, at the above-mentioned temperatures, maximum decomposition rates and percentage weight loss were also established, the values of which are given in table 1. Up to the assumed final temperature of the TGA (600°C),

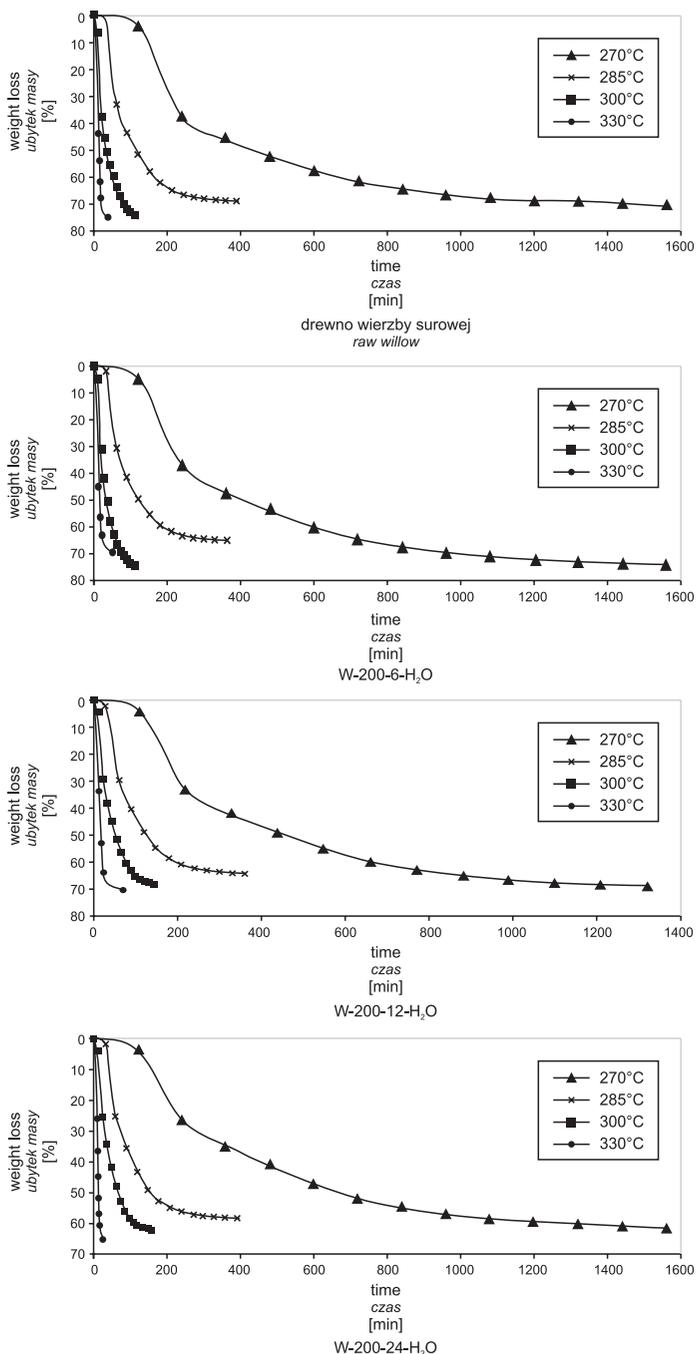
the raw willow wood lost 77.5% of its initial mass. Under identical conditions, the mass loss in the torrefied willow wood was 76.1% for W-200-6-H<sub>2</sub>O, 74.5% for W-200-12-H<sub>2</sub>O and 72.6% for W-200-24-H<sub>2</sub>O.

In comparison to the raw material, the TGA of the torrefied willow wood under polythermal conditions indicates a slight increase in the temperature of the onset of active thermolysis. Moreover, with the duration of the hydrothermal treatment a decrease in the final mass loss, caused by the thermal decomposition of the tested samples, was observed. On the basis of these observations, we may notice an increase in the thermostability of the willow wood with an extension of the modification time.

**Table 1. Thermal characteristic of raw and torrefied willow wood**  
[Czeszejko-Sochacka 2006]

*Tabela 1. Charakterystyka termiczna próbek wikliny surowej i prażonej*  
[Czeszejko-Sochacka 2006]

Sample <i>Rodzaj próbki</i>	Area of active thermolysis <i>Obszar aktywnej termolizy</i> [°C]	Maximum temperature of decomposition rate <i>Temperatura max. szybkości rozkładu</i> [°C]	Maximum decomposition rate <i>Max. szybkość rozkładu</i> [%/min]	Weight loss <i>Ubytek masy</i> [%]	
				in the area of active thermolysis <i>w obszarze aktywnej termolizy</i>	to 600°C <i>do 600°C</i>
raw willow wood <i>wiklina surowa</i>	204-362	263	0.19	58.9	77.5
		334	3.05		
W-200-6-H <sub>2</sub> O	207-360	269	0.97	61.6	76.1
		334	3.54		
W-200-12-H <sub>2</sub> O	210-362	260	0.69	59.4	74.5
		333	3.47		
W-200-24-H <sub>2</sub> O	210-360	263	0.62	56.1	72.6
		333	3.54		



**Fig. 1. TG curves of isothermal decomposition of raw and torrefied willow wood**  
**Rys. 1. Przebiegi krzywych TG podczas izotermicznego rozkładu drewna wierzby surowej i prażonej**

### Thermal decomposition characteristic of raw and torrefied willow wood under isothermal conditions

Data from current literature shows that the beginning of the dynamic decomposition of lignocellulosic materials occurs at 250–270°C [Antal 1985]. Therefore the lower limit of the temperature range in which isothermal (quasi-isothermal) measurements were performed, was established at 270°C. The upper limit for active thermolysis was 320–350°C depending on the process parameters.

On the basis of the analysed TG curves (fig. 1), mass loss limits were found, which these curves ( $m_\infty$ ) approach. It was assumed that these losses are:

- for raw willow wood – 75%,
- for torrefied willow wood W-200-6-H<sub>2</sub>O – 75%,
- for torrefied willow wood W-200-12-H<sub>2</sub>O – 70%,
- for torrefied willow wood W-200-24-H<sub>2</sub>O – 65%.

The times, after which these weight losses are reached, depend on the temperature of decomposition. The higher the decomposition temperature, the faster a tested sample reached the limit value of mass loss.

From the above description it may be concluded that the torrefied willow wood within 24 h is the sample with the greatest thermostability, since it has the lowest weight loss stabilized at 65%. A similar conclusion may be drawn when analysing the thermal characteristics of the raw and torrefied willow wood under dynamic conditions (table 1). Up to a temperature of 600°C, mass loss is lowest also in the case of the torrefied willow wood for 24 h (W-200-24-H<sub>2</sub>O), and amounts to 72.6%.

### Determination of process parameters for the thermal decomposition of raw and torrefied willow wood

The results of the thermogravimetric analyses under isothermal conditions are presented in fig. 1. On their basis a kinetic model which would best describe the experimental data was searched for. The values of the kinetic parameters  $E_a$  and  $A$  of the thermal decomposition process were also calculated.

The calculated values  $E_a$  for the tested material (raw and torrefied willow wood) with respect to selected kinetic models are in the range from 138.1 kJ/mol to 227.3 kJ/mol (table 2). The  $E_a$  values quoted fall within a wide range of the values presented in literature [Alves, Figueiredo 1988; Antal 1985]. The highest  $E_a$  values were calculated for raw and torrefied willow wood at a temperature of 200°C in 24 h.

In the case of the unmodified willow wood, the highest value of  $E_a$  (212.6 kJ/mol) was found for the thermolysis described by model F1. The lowest threshold value of the activation energy (196.3 kJ/mol), which has to be overcome by the tested material, was determined for the reaction of decomposition at the interface

(R3). For the willow wood modified for 6 h (W-200-6-H<sub>2</sub>O), the highest values of  $E_a$  (144.3 kJ/mol) were observed for model R3. For the other two models these values are similar, amounting to approx. 138 kJ/mol. The experimental data shows that for the initiation of pyrolysis in the willow wood modified for 12 h (W-200-12-H<sub>2</sub>O), the required  $E_a$  needs to exceed 139.3 kJ/mol (calculated for model R3). The  $E_a$  for processes F1 and D3 exceeds 150 kJ/mol. The values of  $E_a$  calculated for the torrefied willow wood, W-200-24-H<sub>2</sub>O, are greater than the values of  $E_a$  obtained for the raw willow wood. Among the selected kinetic models, the first order kinetic process (F1) is characterized by the highest value of  $E_a$  of 227.3 kJ/mol. For process D3, the calculated value of  $E_a$  was 222.8 kJ/mol, while for process R3, the value of this energy is lower by almost 11 kJ/mol.

Comparing the  $E_a$  values for model F1, it was observed that these values increase with an extension of the hydrothermal treatment time for the willow wood. The relation was also observed in the case of three-dimensional diffusion (D3) occurring during the pyrolysis of the raw and torrefied willow wood, but it does not occur in the case of the pyrolysis described by kinetic model R3.

The values of the rate constant ( $k$ ), calculated for selected kinetic models, increase with an increasing pyrolysis temperature. In comparison to the material with shorter modification times, the raw material and that subjected to 24h hydrothermal treatment (W-200-24-H<sub>2</sub>O) are characterized by a considerable growth dynamics for the value of parameter  $k$ . The above-mentioned materials (raw willow wood and W-200-24-H<sub>2</sub>O) are also characterized by the highest values of parameter  $E_a$ .

An extension of the torrefaction process time to over 12 h causes an increase in its thermal resistance, resulting in higher  $E_a$  values, calculated for all kinetic models, compared with the raw willow wood. This dependence is confirmed by the thermal characteristic of the willow wood. The above shows that the material modified for the longest is characterized by the lowest value of mass loss at the final temperature of pyrolysis, i.e. at 600°C.

The numerical values of the pre-exponential coefficient ( $A$ ) increase with the increasing value of activation energy, which indicates the existence of the so-called compensation effect. In accordance with the theory of active collisions, when calculating the value of  $E_a$ , the level of the energy limit is determined, which needs to be overcome. This stage has to limit the rate of the summary thermal dissociation process. Parameter  $A$  is defined as the frequency of such a configuration of molecules, which is advantageous for the occurrence of the reaction [Agrawal 1985].

Table 2 presents the values of the pre-exponential coefficient ( $A$ ). The cited values are contained within the range of  $1.19 \cdot 10^{10} \text{ min}^{-1}$  (model D3 W-200-6-H<sub>2</sub>O) to  $1.27 \cdot 10^{19} \text{ min}^{-1}$  (model F1 W-200-24-H<sub>2</sub>O).

Parameter  $A$ , calculated for selected kinetic models describing the process of thermolysis in the raw willow wood, increases in value with an increase in  $E_a$ .

The lowest value of parameter  $A$  ( $3.38 \cdot 10^{15} \text{ min}^{-1}$ ) was found for kinetic model R3. For the first order kinetic process (F1), the highest value of  $E_a$  was recorded and thus the greatest value of the pre-exponential coefficient  $A$  ( $6.17 \cdot 10^{17} \text{ min}^{-1}$ ). A similar dependence was observed in the case of the parameters  $A$  and  $E_a$  calculated for the willow wood modified for 12 h (W-200-12-H<sub>2</sub>O). The highest value of  $E_a$  (model F1) corresponds to the greatest value of parameter  $A$ .

Comparing the numerical data of parameters  $A$  and  $E_a$  recorded for the willow wood subjected to 24 h hydrothermal treatment (W-200-24-H<sub>2</sub>O), the above-mentioned dependence was also observed. In the discussed case, the value of the pre-exponential coefficient ( $A$ ) increases with an increase in the value of parameter  $E_a$  (table 2).

An analogous dependence was not observed in the case of parameters  $A$  and  $E_a$  calculated for the willow wood modified thermally for 6 h (W-200-6-H<sub>2</sub>O). The lowest value of energy  $E_a$  (model F1) is connected here with the highest value of parameter  $A$  (table 2).

**Table 2. The values of rate constant  $k$  of the thermal decomposition process of raw and torrefied willow wood and the kinetic parameters: activation energy ( $E_a$ ) and pre-exponential coefficient ( $A$ ) for the selected kinetic models**

*Tabela 2. Wartość stałych szybkości  $k$  procesu termicznego rozkładu wierzby surowej i prażonej oraz parametry kinetyczne: energia aktywacji ( $E_a$ ) i współczynnik przedwykładniczy ( $A$ ) dla wybranych modeli kinetycznych*

Sample <i>Rodzaj próbki</i>	Kinetic model <i>Model kinetyczny</i> 270°C	$k$				$E_a$ (kJ/mol)	$A$ (min <sup>-1</sup> )
		285°C	300°C	330°C			
Raw willow wood <i>Wilkłina surowa</i>	F1	0.001741	0.006785	0.04865	0.1725	212.6	$6.17 \cdot 10^{17}$
	D3	0.0002568	0.0009847	0.006616	0.02396	209.6	$4.58 \cdot 10^{16}$
	R3	0.0003495	0.001400	0.006945	0.02572	196.3	$3.38 \cdot 10^{15}$
W-200-6-H <sub>2</sub> O	F1	0.003040	0.005797	0.04400	0.05186	138.1	$6.97 \cdot 10^{10}$
	D3	0.0004437	0.0007898	0.006368	0.007545	138.9	$1.19 \cdot 10^{10}$
	R3	0.0004854	0.001309	0.007313	0.01055	144.3	$4.86 \cdot 10^{10}$
W-200-12-H <sub>2</sub> O	F1	0.003232	0.007327	0.02655	0.09539	157.1	$4.28 \cdot 10^{12}$
	D3	0.0004778	0.001051	0.003949	0.01228	151.2	$1.75 \cdot 10^{11}$
	R3	0.0005500	0.001537	0.004892	0.01185	139.3	$1.70 \cdot 10^{10}$
W-200-24-H <sub>2</sub> O	F1	0.001942	0.005990	0.02149	0.2794	227.3	$1.27 \cdot 10^{19}$
	D3	0.0002852	0.0008424	0.003178	0.03666	222.8	$6.92 \cdot 10^{17}$
	R3	0.0003888	0.001301	0.004171	0.04124	211.9	$9.02 \cdot 10^{16}$

### Criterion values for the selection of the kinetic model

Table 3 presents the values of criterion numbers useful in the selection of a kinetic model with the best fit to the experimental data. Comparing the results of the calculations for the criterion number  $\Sigma S$  for different kinetic models, it may be stated that its lowest values were calculated for the first order kinetic process (F1), occurring during the thermolysis of the raw willow wood as well as the willow wood modified for 6 and 12 h. In view of the value of  $\Sigma S$  for the longest torrefied willow wood (W-200-24-H<sub>2</sub>O), model R3 seems to be the model with the best fit.

An analysis of the values of the mean correlation coefficients ( $\bar{x}r^2$ ) indicates model D3 as the one best describing the experimental data, except for the material after 12 h of hydrothermal treatment (W-200-12-H<sub>2</sub>O). Thus this model may be proposed for the description of the kinetics of pyrolysis in raw and torrefied willow wood. This statement is consistent with the considerations of Zakrzewski [2001] on the kinetics of thermolysis in lignocellulosic materials.

**Table 3. The values of the mean correlation coefficients ( $\bar{x}r^2$ ) and the sum of  $S$  criterion based on the linearization  $g(\alpha)$  of time for the selected kinetic models of the isothermal decomposition of raw and torrefied willow wood**

*Tabela 3. Wartości średnich współczynników korelacji ( $\bar{x}r^2$ ) i sumy kryterium  $S$  przy linearyzacji zależności  $g(\alpha)$  od czasu dla wybranych modeli kinetycznych procesu izotermicznego rozkładu wierzby surowej i prażonej*

Sample <i>Rodzaj próbki</i>	Kinetic model <i>Model kinetyczny</i>	$\bar{x}r^2$	$\Sigma S$
Raw willow wood <i>Wilkina surowa</i>	F1	0.9630	0.8511
	D3	0.9770	1.5067
	R3	0.9553	1.4053
W-200-6-H <sub>2</sub> O	F1	0.9593	0.6348
	D3	0.9700	1.2002
	R3	0.9393	1.6163
W-200-12-H <sub>2</sub> O	F1	0.9855	0.4229
	D3	0.9848	1.2918
	R3	0.9503	1.0934
W-200-24-H <sub>2</sub> O	F1	0.9684	0.9515
	D3	0.9790	1.8292
	R3	0.9600	0.9433

Based on the analysis of experimental and theoretical curves illustrating a dependence of the degree of transformation  $\alpha$  on time  $t$ , calculated on the basis of  $E_a$  and  $A$  for different kinetic models, it was found that models F1 and D3 are those best describing the course of thermolysis in willow wood. Model R3 is the model most divergent from the experimental data.

## Conclusions

The course of the thermal decomposition of raw and torrefied willow wood under iso- and polythermal conditions indicates the highest thermal resistance of willow wood subjected to 24 h hydrothermal treatment. The numerical values of activation energy  $E_a$  depend on the growth dynamics for rate constant  $k$  in the function of temperature. An extension of the hydrothermal treatment time increases the thermal resistance of torrefied willow wood, which results in a lower mass loss during thermolysis and an increase in  $E_a$  of this process. The value of the pre-exponential coefficient  $A$  increases with an increase in activation energy. The application of criteria  $\Sigma S$  and  $\bar{x}r^2$  objectifies the selection of the model best describing the course of the thermal decomposition of raw and torrefied willow wood. The kinetic model D3 is the model which best describes the course of thermolysis in raw and torrefied willow wood.

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## **BADANIA KINETYKI PROCESU TERMICZNEGO ROZKŁADU DREWNA WIERZBY KONOPIANKI (*SALIX VIMINALIS* L.) PODDANEGO OBRÓBCE HYDROTERMICZNEJ**

### **Streszczenie**

Celem pracy było obliczenie parametrów kinetycznych (energii aktywacji  $E_a$ , współczynnika przedwykładniczego  $A$ , stałej szybkości  $k$ ) procesu termolizy prażonego i surowego drewna wierzby konopianki (*Salix viminalis* L.) oraz określenie wpływu warunków modyfikacji termicznej na kinetykę tego procesu.

Stosowano próbki wikliny surowej oraz prażonej w następujących warunkach: temperatura procesu 200°C, czas prażenia: 6 godzin (W-200-6-H<sub>2</sub>O), 12 godzin (W-200-12-H<sub>2</sub>O) oraz 24 godziny (W-200-24-H<sub>2</sub>O). Proces był prowadzony w atmosferze pary wodnej, działającej przez 6 godzin w początkowym okresie modyfikacji. Surowce poddano analizie termogravimetrycznej w warunkach izotermicznych. Analizy były prowadzone w atmosferze helu w temperaturach 270°C, 285°C, 300°C, 330°C. Rejestrowano krzywe TG i DTG. Charakterystykę termiczną wikliny oparto na analizie termogravimetrycznej w warunkach dynamicznych, w temperaturze do 600°C.

Na podstawie danych otrzymanych z wykonanych analiz obliczono parametry kinetyczne ( $E_a$ ,  $A$ ,  $k$ ) i przeprowadzono analizę statystyczno-matematyczną wyników.

Wartość energii aktywacji procesu termolizy wikliny zawierała się w przedziale 138,1–227,3 kJ/mol. Największą wartość  $E_a$  (227,3 kJ/mol) uzyskano w przypadku wikliny prażonej w temperaturze 200°C, w czasie 24 godzin (W-200-24-H<sub>2</sub>O). Surowiec ten również okazał się najbardziej odporny termicznie.

W celu ustalenia funkcji  $g(\alpha)$ , która najlepiej opisuje proces termicznego rozkładu surowego i prażonego drewna wierzby konopianki wybrano trzy modele kinetyczne: F1, D3, R3. Modelem, który najlepiej opisywał dane doświadczalne był model D3, odnoszący się do procesu dyfuzji trójwymiarowej.

**Słowa kluczowe:** analiza termiczna, rozkład termiczny, piroliza, kinetyka, prażenie drewna, toryfikacja

