



The non-isothermal thermogravimetric tests of animal bones combustion. Part II. Statistical analysis: Application of the Weibull mixture model

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ABSTRACT

The possibility of applying the Weibull mixture model for the fitting of the non-isothermal conversion data for the combustion process of animal bone samples has been investigated. It has been found that the conversion data at the different heating rates for the investigated samples, can be successfully described by the linear combination of few Weibull distribution functions. An optimal fitting of the conversion data has been obtained by a mixture of three Weibull distribution functions. It was established that the conversion curves calculated by the proposed model, are in good agreement with the raw conversion data of the investigated bone samples. The alterations of distribution parameters in the Weibull mixture model, indicate a probably change of the kinetic nature of the particular reaction stage. A model with a continuous distribution of the apparent activation energies (E_a) can adequately represents the individually stages of the complex combustion process. The characterization of the estimated distribution curves, enable us to receive the additional information's about the kinetic behaviour of individual reaction stages, which does not attainable from the results of conventional kinetic analysis.

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1. Introduction

Bone is a composite material comprised of an organic matrix and an inorganic crystalline mineral component. The mineral component has a structure which is related to that of the mineral hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP). On heat treatment of bone to high temperatures, the organic components of bone are removed through combustion and the inorganic component undergoes recrystallization and thermal decomposition.

In our previous paper [1] we are investigated the non-isothermal combustion process of animal (bovine) bones in air atmosphere. The full kinetic triplet (pre-exponential factor (A), apparent activation energy (E_a) and function of reaction mechanism ($f(\alpha)$) for the investigated process was established [1]. It was found that the combustion process of bone sample is a complex one, which exhibits three reaction stages (designated as stage I, II and III), with the different kinetic mechanisms. In addition, because the compensation coefficients corresponding to the all three reaction stages are different, it was concluded that the considered reaction stages cannot be unified by simple kinetic model [1].

In present paper, the possibility of applying the Weibull mixture model for fitting of the non-isothermal kinetic conversion curves for the investigated combustion process was established.

The mixed Weibull distribution provides a flexible model to analyze the possible changes in the rate-limiting step (for example, from autocatalytic to n th order reaction) of complex heterogeneous process. The observed changes in the rate-limiting step of considered complex process can be easily detected from the alteration of shape parameter in the Weibull mixture model.

In this paper, mixtures of three Weibull distributions are applied in the context of modelling the kinetic data for combustion process of animal bone samples.

The non-isothermal conversion ($\alpha - T$) curves can be obtained through the non-isothermal analysis. Different authors have stated that the use of the differential conversion ($d\alpha/dT - T$) curves instead of the conversion curves makes easier the identification of the kinetics [2–4], mainly because small changes in the conversion curves are magnified in the corresponding differential conversion curves. Also, the small errors in the conversion curves are magnified in the differential conversion curves. There are some high fluctuations in the differential conversion curves, and some filtrations of the data are needed for smooth curves. A large number of smoothing algorithms have been developed, ranging from a polynomial algorithm to the Gaussian smoothing algorithm [5–7]. The kinetic analysis of complex reactions, such as overlapping reactions, has received the attention of a great number of authors [8–10]. Overlapping reactions could be detected looking at the dependence of the apparent activation energy (E_a) on the extent of conversion (α) [11]. To separate the individual steps of complex processes, many methods have been proposed [12–17].

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Table 1Values of bone sample mass before and after of annealing procedure performed at the different temperatures: $T=400$ °C, 500, 600, 700, 800 and 900 °C.

Bone samples	Initial mass (g)	Mass after 4 h of annealing at contributed temperature (g)	Mass (%)
Raw bone	70.00	70.00	100
Bone $T=400$ °C	70.00	48.50	69.28
Bone $T=500$ °C	70.00	47.15	67.35
Bone $T=600$ °C	70.00	45.29	64.70
Bone $T=700$ °C	70.00	44.56	63.65
Bone $T=800$ °C	70.00	43.16	61.65
Bone $T=900$ °C	70.00	42.85	61.21

Concerned about overcoming the smoothing problem when analyzing the non-isothermal data and problem of clearly separating of individual reaction steps in the complex process, in this paper we aim to show a statistical method to model the non-isothermal kinetic conversion data of bone combustion, by the linear combination of few Weibull distribution functions. The Weibull distribution's popularity resulted from its ability to be used with small data sets and its flexibility. Example of the above statement was given by Kolar-Anić et al. [18,19], which applied the Weibull distribution function for the kinetically explanations of different heterogeneous processes.

The mixed Weibull distribution is a probability mixture of Weibull distributions which differ in scale and/or shape parameter. Titterton et al. [20] point out that the mixture distributions have been used as models throughout the history of modern statistics and give a detailed list of references on applications of mixture models. Jiang [21] gives a detailed literature review on Weibull mixture models. Also, the application of mixed Weibull distributions can also be seen in works of Lancaster [22] and Lindsay [23]. Cai and Liu [24], applied the Weibull mixture model for the kinetic curves description of an epoxy-hexahydrophthalic anhydride degradation and the thermal decomposition of foamed polyurethane in air atmosphere. Also, Cai and Alimujiang [25] are used the Weibull and logistic mixture models for fitting the kinetic conversion data calculated from thermogravimetric (TG) measurements, during wheat straw oxidative pyrolysis. The statistical results showed that the Weibull mixture model fitted the experimental data better than the logistic mixture model and can accurately reproduce the kinetic conversion data.

In this paper, the mixed Weibull distribution model was applied for modelling the kinetics of non-isothermal combustion process of animal bone samples.

2. Experimental procedure

2.1. Bone samples

The sample used in this study originated from bovine (femur) bones. Bones were cleaned from meat, cut into smaller pieces, boiled in distilled water in order to remove fat and subsequently dried in the oven at 80 °C. Fraction of particle size 45–200 μm , obtained by milling and sieving, was used for the TG–DTA measurements. The details about sample preparation and characterization are published elsewhere [26].

2.2. Thermal measurements

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on STA-1000 Simultaneous Thermal Analyzer, Stanton Redcroft, UK. The bone samples with approximately $m \approx 5$ –10 mg were heated at three different heating rates $\beta = 2.5, 5$ and 20 °C min^{-1} , in air atmosphere (air flow $\varphi = 20$ ml min^{-1}) in the temperature range of $\Delta T = 20$ –650 °C.

Table 1 shows the results of residual mass of bovine bone samples (including the raw bone sample) after 4 h of annealing at the six different temperatures ($T = 400, 500, 600, 700, 800$ and 900 °C).

It can be observed from Table 1 that the mass of bone sample (starting from the raw bone sample) manifests the progressive decreasing with increasing of temperature. At the higher annealing temperature ($T = 900$ °C), the value of mass loss is the largest (Table 1). These results are in good agreement with mass loss values detected from the experimentally obtained thermogravimetric (TG) curves of the investigated bone samples [1] at the considered temperatures (Table 1).

3. Weibull mixture model

The model proposes decomposition of a non-isothermal conversion curve into several Weibull distribution functions, assuming that decomposition kinetics of each component of the sample is represented by one or the sum of few functions. Even in the case of homogeneous materials, it is supposed that several different structures may exist, each one following its specific kinetics that may be different from the others [15,16].

In this mathematical model, it is assumed that a kinetic conversion curve may be fitted by one or the linear combination of few Weibull distribution functions:

$$\alpha(T) \equiv F(T) = \sum_{i=1}^m w_i \left(1 - \exp \left[- \left(\frac{T - T_0}{v_h \eta_i} \right)^{\beta_i} \right] \right) \quad (1)$$

where $i = 1, 2, \dots, m$ represent different components from the kinetic conversion process, not necessarily different chemical compounds, $F(T)$ is the cumulative probability function of the Weibull m -mixture (where $\alpha(T)$ is the extent of conversion under non-isothermal conditions, identical to $F(T)$), T is the temperature ($T \geq T_0$, T_0 is the onset temperature of the process and acts as the location parameter of the Weibull distribution function), w_i stands for the weight of the i th component of the Weibull mixture model, η_i is the scale parameter of the i th Weibull distribution function, where $\eta_i > 0$, β_i is the shape parameter of the i th Weibull distribution function, where $\beta_i > 0$, and v_h is the linear heating rate. According to the dimensional analysis, β_i is expressed in dimensionless, and η_i is expressed in min. If the components follow the Weibull distribution, the investigated system would follow the proposed Weibull mixture model allowing positive weights. In addition, Eq. (1) can be shortly written as $MW(m, \beta, \eta, w_1, \dots, w_{m-1})$. A pure Weibull distribution ($m = 1$) is denoted by $W(\beta, \eta)$.

When $T \rightarrow \infty$, the value of $\alpha(T)$ function has to tend to 1. Therefore, from Eq. (1), the following relation can be obtained:

$$\sum_{i=1}^m w_i = 1 \quad (2)$$

Additionally, the reaction rate of the Weibull m -mixture model process can be given by the first derivative of Eq. (1) with respect

to temperature. The obtained function represent, the continuous probability density function (p.d.f.) of reaction temperatures at a given heating rate of the system. In that case, the following relation is valid:

$$\frac{d\alpha}{dT} \equiv f(T | \beta_i; \eta_i) = \sum_{i=1}^m w_i \frac{\beta_i}{\eta_i v_h} \left[\frac{T - T_0}{\eta_i v_h} \right]^{\beta_i - 1} \exp \left[- \left(\frac{T - T_0}{\eta_i v_h} \right)^{\beta_i} \right] \quad (3)$$

where constants β_i and η_i stand for Weibull shape and scale parameters of the component densities. They are limited according to the characteristics of the Weibull distribution $\beta_i > 0$ and $\eta_i > 0$ for $i = 1, \dots, m$.

3.1. Estimation of distribution parameters

For fitting the non-isothermal conversion data with Weibull mixture model, some estimation of the parameters in Eq. (1) is needed. To evaluate the parameters, the residual sum of squares of deviations of actual and calculated values is commonly used. It is defined by the following equation [27]:

$$RSS = \sum_{j=1}^n (\alpha_{ac,j} - \alpha_{calc,j})^2 \quad (4)$$

where $\alpha_{ac,j}$ is the actual value of the extent of conversion in the data point j , $\alpha_{calc,j}$ is the value calculated from Eq. (1) in the corresponding point, and n is the number of data points.

There are a number of algorithms for minimizing the Eq. (4) enabling us to find best values of the parameters. The fundamentals of the optimization methods were described in detail form by Jongen et al. [28]. In this study, the Levenberg–Marquardt method has been used for the calculation of the values of the parameters that minimize Eq. (4). This method represent non-linear optimization, which minimizes the function that is a sum of squares of non-linear functions. Many methods use the gradient of the function to be minimized. From the mathematical point of view, the Levenberg–Marquardt method uses a Jacobian instead of gradient [29].

For performing the Levenberg–Marquardt method, either general purposed mathematical software or a computer program developed in any programming language is used. In this study, the OriginLab 8.5[®] software (Advanced Visual Version (C++) (AVVC)) program has been employed for performing the ideal optimization procedure.

One of the problems that appear when using the method is to choose some initial values for the parameters to estimate [15]. One of the easier method for estimation of the Weibull model parameters, represents the double logarithmic plot (DLP) method or the Weibull probability plot method. In that manner, we have proposed a method based on the idea of assuming that the data follow one Weibull distribution function (see Eq. (1)). In that sense, we use the linear form of Eq. (1) ('lnln' plot), given by the following relation:

$$\ln[-\ln(1 - \alpha(T))] = \beta \ln \left(\frac{1}{\eta} \right) + \beta \ln \left[\frac{T - T_0}{v_h} \right] \quad (5)$$

The values of distribution parameters β and η would be obtained from the slope and the intercept of the plot of $\ln[-\ln(1 - \alpha(T))]$ vs. $\ln[(T - T_0)]/v_h$.

4. Distributed activation energy model (DAEM)

The distributed activation energy model (DAEM) has been proved successful in describing the decomposition kinetics of various complex materials, such as coal [30] and oil shale [31]. The model assumes that the distribution of reactivity can be described

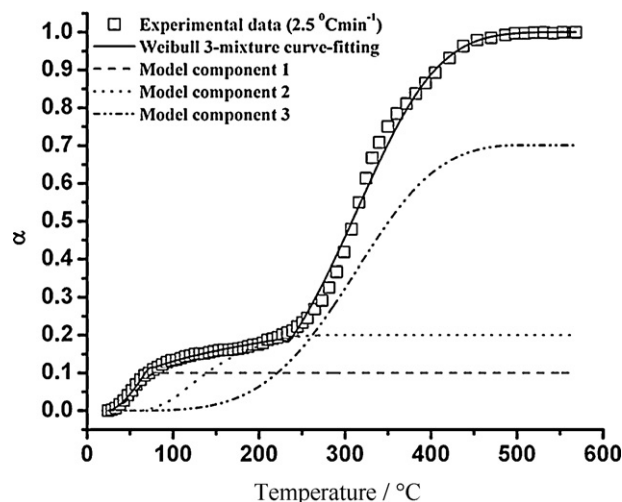


Fig. 1. Overlay of the raw data, the Weibull 3-mixture curve-fitting and the single model components obtained by the fitting procedure, in the case of the bone combustion process in air atmosphere at 2.5 °C min⁻¹.

by a set of independent and parallel reactions, each with its own pre-exponential factor and the apparent activation energy. Usually, it is further assumed that all reactions share the same pre-exponential factor, so the reactivity distribution is represented by a continuous distribution of the apparent activation energies [32]. Therefore, the corresponding model of reactivity and the kinetic parameters will fit a larger range of reaction temperatures than the single reaction model [32].

Previous studies assumed only a Gaussian distribution of the apparent activation energies [33–36]. However, this assumption may be questionable when the apparent activation energy values are widely distributed, in which case the pre-exponential factors do not necessarily remain constant [37]. In this work, the Miura's [38,39] computational procedure was used to estimate the distribution function $g(E_a)$, which is obtained by the differentiation of the $\alpha(E_a)$ function with respect to the apparent activation energy:

$$g(E_a) = \frac{d\alpha(E_a)}{dE_a} \quad (6)$$

The $\alpha(E_a)$ function, that relates the total extent of conversion with the apparent activation energy, is calculated from the experimental data of α vs. T ; the Arrhenius (kinetic) parameters are calculated for each conversion at the different heating rates [1]. It can be pointed out, that Braun and Burnham [40] clarified that the conversion-dependent E_a values obtained by Friedman's isoconversional method [2] result from the distribution of the apparent activation energy. This is the correct interpretation because conversion-dependent E_a values actually are obtained by Friedman's method when E_a is assumed to be a function of α [1].

5. Results and discussion

The experimental conversion data of combustion process of bone sample was obtained from our previous paper [1], based on the thermogravimetric (TG) measurements. The experiments were performed using a linear heating regime, at the different rates ($v_h = 2.5, 5$ and 20 °C min⁻¹) in air atmosphere. The realised experiments are showed that the investigated combustion process of bone samples occurs through the three reaction stages, giving a complex conversion curve at all heating rates (Figs. 1–3).

The best fitting of experimental results was obtained with three Weibull distribution functions at all heating rates, and consider-

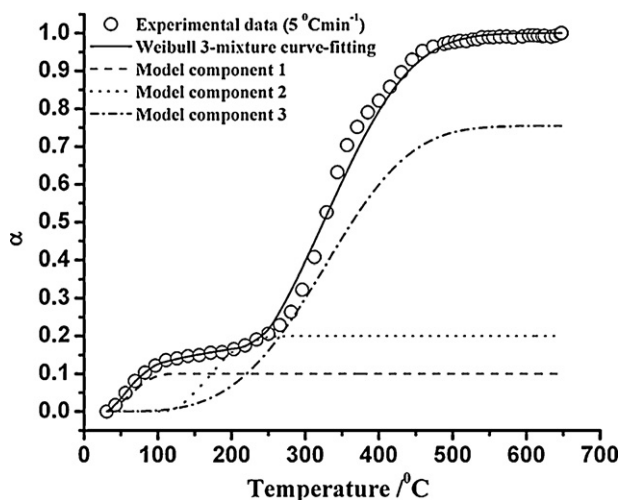


Fig. 2. Overlay of the raw data, the Weibull 3-mixture curve-fitting and the single model components obtained by the fitting procedure, in the case of the bone combustion process in air atmosphere at $5^{\circ}\text{C min}^{-1}$.

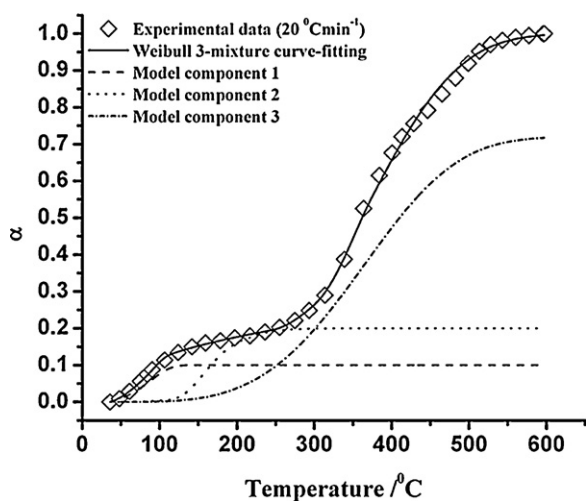


Fig. 3. Overlay of the raw data, the Weibull 3-mixture curve-fitting and the single model components obtained by the fitting procedure, in the case of the bone combustion process in air atmosphere at $20^{\circ}\text{C min}^{-1}$.

ing the residual standard error, a higher number does not improve significantly the quality of the fitting.

The estimated parameters are listed in Table 2. From Table 2, we have that $\beta_1 > \beta_2 < \beta_3$ and $\eta_1 < \eta_2 > \eta_3$ at all heating rates, which indicates that the reaction mechanism for the second stage of the investigated process is significantly different from the others. This statement is confirmed in our previous paper [1]. Figs. 1–3 show the overlay of the raw data, the Weibull mixture curve-

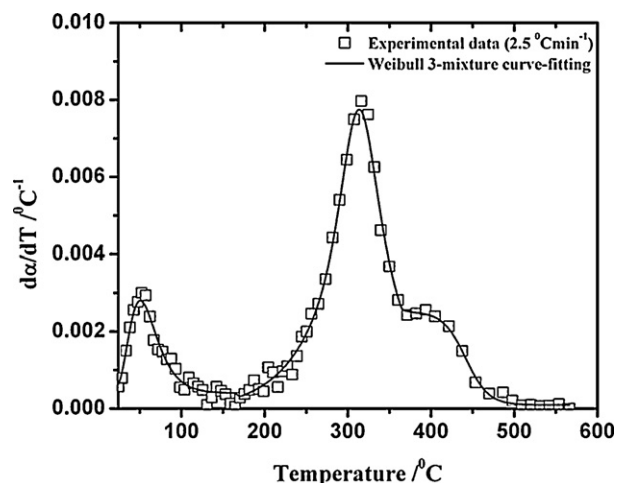


Fig. 4. The comparison of the experimentally obtained non-isothermal rate curve ($d\alpha/dT$ against T) (symbol \square) and the calculated rate curve using Eq. (3) (the probability density function), which represents the Weibull 3-mixture curve-fitting for the investigated bone combustion process.

fitting, and the single model components obtained by the fitting procedure.

It can be seen from Figs. 1–3 that a good match between the experimental data and the fitted model can be obtained. It was concluded [1] that the first, second and third stage corresponds to the dehydration, degradation and combustion processes, respectively. The first reaction stage can be described by the reaction model, which contains competing reactions with different values of the apparent activation energy [1]. In addition, it was established, that the autocatalytic two-parameter Šesták–Berggren (SB) model can best describes the second stage of the investigated process [1]. The complexity of the investigated process can be easily verified by comparing the experimental rate curves in the form of $d\alpha/dT$ vs. T and the numerically evaluated rate curves, using Eq. (3) and results from Table 2, which represent the Weibull 3-mixture curve-fitting approach.

The Weibull mixture model [41,42] can be used for smoothing procedure of the differential conversion data obtained by experimental means [24,25].

Fig. 4 shows the comparison of the experimentally obtained non-isothermal rate curve ($d\alpha/dT$ against T) and the calculated rate curve using Eq. (3) (the probability density function), which represents the Weibull 3-mixture distribution model, with corresponding parameters from Table 2. The comparison is achieved at the heating rate of $\nu_h = 2.5^{\circ}\text{C min}^{-1}$. It can be seen from Fig. 4, that the excellent agreement exists between the observed reaction rate curves expressed as $d\alpha/dT$ vs. T at the considered heating rate. The similar results are obtained for the other values of heating rates (for $\nu_h = 5$ and $20^{\circ}\text{C min}^{-1}$). Making use of the data fitted by the Weibull mixture model, some data required for the isoconversional

Table 2

Values of the parameters of the Weibull mixture model obtained in the case of three-stage combustion process of the bovine bone samples.

Heating rate, ν_h ($^{\circ}\text{C min}^{-1}$)	Stage	Components	β_i	η_i (min)	w_i	RSS ^a
2.5	I	1	1.61708	69.58942	0.80112	0.01951
	II	2	0.41397	3504.38223	0.10125	
	III	3	4.12863	124.06948	0.09763	
5	I	1	1.27143	55.95971	0.72563	0.02542
	II	2	0.32684	6340.47059	0.17110	
	III	3	3.62939	65.06181	0.10327	
20	I	1	1.49098	13.66867	0.70445	0.00335
	II	2	0.44882	315.45741	0.18524	
	III	3	3.78333	14.19446	0.11031	

^a Residual sum of squares.

Table 3
Values of the polynomial coefficients evaluated for the second (II) reaction stage of the bone combustion process at the different values of heating rates: $v_h = 2.5, 5$ and $20^\circ\text{C min}^{-1}$.

v_h ($^\circ\text{C min}^{-1}$)	c_0	c_1	c_2	c_3	c_4	c_5	R^a
2.5	-0.02496	0.31614	-1.56517	4.49317	-5.92300	2.76389	0.99740
5	-0.00763	0.01501	0.23832	0.57685	-2.26665	1.48533	0.99723
20	0.13272	-2.38266	14.06323	-30.81616	28.95851	-9.98083	0.99545

^a Linear correlation coefficient.

kinetic analysis, such as α vs. T_α or $(d\alpha/dT)$ vs. $1/T_\alpha$ (Fig. 4), can be obtained. Based on the fitting of Weibull mixture model, the apparent activation energy values (E_a) can be calculated using Friedman's differential isoconversional method [43].

Mathematical descriptions of the various types of reaction process are available. The experimental data of the non-isothermal experiment can be fitted to the most appropriate form and the kinetic parameters deduced via mathematical manipulation of the data. The empirical kinetics can be used to describe a process when the aim is to utilize the model as a predictive tool rather than to determine the reaction mechanisms [44].

An alternative empirical method use the polynomial function with a suitable number of terms to approximate the kinetic function as in Eq. (7):

$$v_h \frac{d\alpha}{dT} = c_0\alpha^p + c_1\alpha^{p+1} + c_2\alpha^{p+2} + \dots \quad (7)$$

If we extricate the term $c_0\alpha^p$ from the right-hand side of Eq. (7), we obtain the following equation:

$$v_h \frac{d\alpha}{dT} = c_0\alpha^p \left(1 + \frac{c_1}{c_0}\alpha + \frac{c_2}{c_0}\alpha^2 + \dots \right) \quad (8)$$

However, Eq. (8) can be reduced to a simpler expression as:

$$v_h \frac{d\alpha}{dT} \propto \alpha^m (1 - \alpha)^n \quad (9)$$

which represents the empirical two-parameter autocatalytic Šesták–Berggren reaction model. The exponent n is normally an integer for simple reactions ranging from 0 to 3 and refers to the number of molecules involved in collisions that lead to a reaction. In contrast to homogeneous reactions, for heterogeneous reactions fractional reaction orders are often observed. Fractional orders signify complexity of the process and that the chosen model is thereby empirical. For the second stage of bone combustion process, the value of n higher than 3 ($n > 3$) was obtained ($n = 3.22$) [1]. This result indicates a more complex degradation process of organic phase in the investigated bone sample.

Fig. 5 shows the comparison of the experimentally obtained rate curves and corresponding 5th order polynomial fits for the second stage of bone combustion process at considered heating rates.

It can be seen that exist very good agreement between the experimentally obtained and polynomial expressed reaction rate curves for the second reaction stage. The corresponding polynomial coefficients evaluated for the second reaction stage at considered heating rates are presented in Table 3.

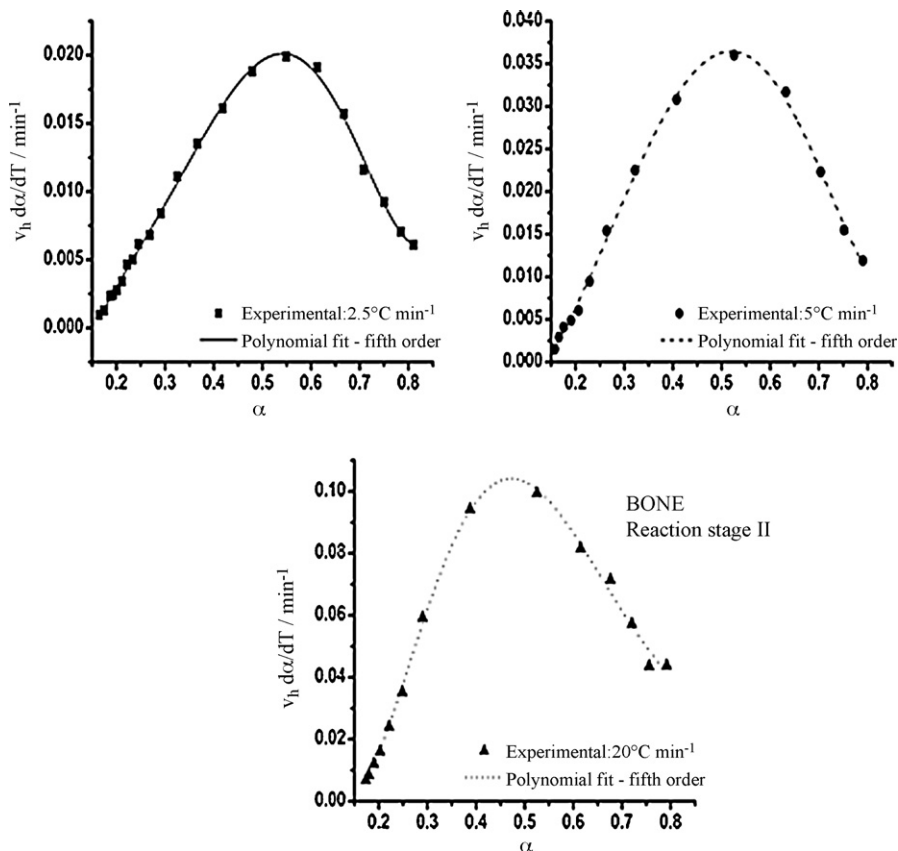


Fig. 5. The comparison of experimentally obtained rate curves and corresponding 5th order polynomial fits for the second (II) stage of the bone sample combustion process at the considered heating rates.

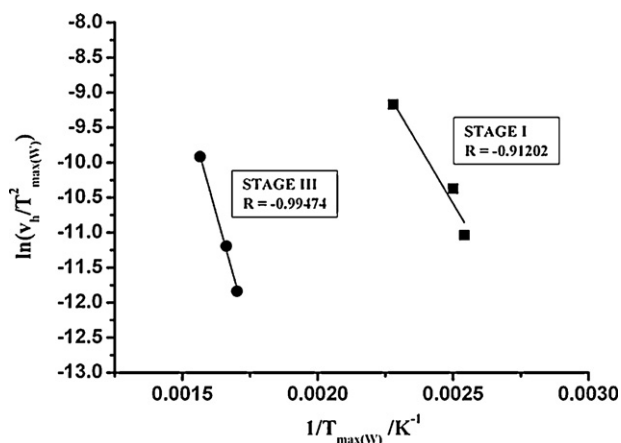


Fig. 6. The Kissinger plots of $\ln(v_h/T_{\max(W)}^2)$ vs. $1/T_{\max(W)}$ for the first (I) and third (III) reaction stage of the bone combustion at the considered heating rates (R = linear correlation coefficient).

These results confirm that the reaction model expressed through the autocatalytic kinetic equation (Eq. (9)) is the best reaction model for describing the degradation process of organic components (mainly collagen) in bone sample [1].

The third reaction stage corresponds to the combustion process of the organic components, which arise from the degradation of collagen molecule. This reaction stage can be best described by an n th reaction order (RON) model with $n = 1.5$ ($v_h d\alpha/dT \sim (1 - \alpha)^{1.5}$) [1].

The value of maximum temperature, which corresponds to the maximum rate, can be obtained when the first derivative of Eq. (3) is equal to zero, and this value is given by the following relation:

$$T_{\max(W)} = v_h \eta \left(\frac{\beta - 1}{\beta} \right)^{1/\beta} + T_0 \quad (10)$$

where we assumed that $T_{\max(W)}$ value follow one Weibull distribution function. Values of $T_{\max(W)}$ calculated at particular heating rate (Eq. (10)), can be used for calculation of the apparent activation energy (E_a) for corresponding reaction stages of bone combustion process. The Kissinger equation [45] in which temperature $T_{\max(W)}$ is defined from Eq. (10), enable us to calculate the value of E_a as

$$\ln \left(\frac{v_h}{T_{\max(W)}^2} \right) = \ln(C_f) - \frac{E_a}{RT_{\max(W)}} \quad (11)$$

where v_h is the heating rate, C_f is the constant and E_a is the value of the apparent activation energy for corresponding values of the maximum temperature ($T_{\max(W)}$).

The Kissinger plots (Eq. (11)) obtained for the first and third reaction stage of bone sample, with corresponding linear correlation coefficient values (R), are presented in Fig. 6.

Table 4 shows the values of the apparent activation energy (E_a) calculated from the experimental TG–DTA curves [1] and from Eq. (11) using the values of $T_{\max(W)}$ in the Eq. (10), for the first and third reaction stage of the investigated bone samples.

We can see from Table 4, that the values of E_a for the first reaction stage are in good agreement. However, if we look at Fig. 6, we note that the linear correlation coefficient is very poor ($R = -0.91202$). Therefore, the value of E_a resulting from the Eq. (11) for $T_{\max(W)}$ values calculated using Eq. (10) should not be considered as a reliable value. On the other hand, the value of the linear correlation coefficient for third reaction stage (Fig. 6) is quite satisfactory ($R = -0.99474$), but the value for E_a obtained using Eq. (11) differs significantly from the value of E_a calculated from the experimental TG–DTA curves [1]. The reason for these differences in the values of

Table 4

The values of the apparent activation energy (E_a) calculated from the Kissinger equation, using the values of T_{\max} determined from the experimental TG–DTA curves [1] and from the Eq. (11) using the values of $T_{\max(W)}$ in Eq. (10), for the corresponding reaction stages of bovine bone combustion process.

Reaction stage	Bovine bone sample	
	E_a (kJ mol ⁻¹) ^a	E_a (kJ mol ⁻¹) ^b
I	53.7 ± 0.7	54.3 ± 1.4
II	–	–
III	138.6 ± 1.9	115.6 ± 0.8

^a E_a value calculated from the Kissinger equation, using the values of T_{\max} determined from the experimental TG–DTA curves [1].

^b E_a value calculated from the Eq. (11), using the values of $T_{\max(W)}$ determined from Eq. (10).

E_a lies in the appearance of the second term in Eq. (10) (the onset temperature, T_0). Namely, the corresponding value of the onset temperature can, to the implicit way, bring the significant error in calculating E_a using Eq. (11). Thus, Eq. (11) is not suitable for the calculation of E_a values due to uncertainty in the $T_{\max(W)}$ values. Another reason for these differences in the values of E_a may come from the strong influence of heating rate on the values of distribution parameters (β and η) (Table 2). This influence can be eliminated in the procedure of determining the values of distribution parameters, for the case of introduced approximation when the heating rate approaches zero [46].

Fig. 7 shows the plotting of the $\alpha(E_a)$ function, which is derived using the Friedman's isoconversional method, where the procedure is based on the Weibull 3-mixture curve-fitting approach (Figs. 1–4).

It is observed that as the conversion increases (from $\alpha = 0.05$ to $\alpha = 0.15$), the energy barrier that must be surpassed is higher. This result due to the water molecules which are strongly bounded in bone structure, and in such a manner the higher value of E_a is needed for their liberation. It was found that the obtained values of E_a (from $E_a = 70.2$ kJ mol⁻¹ to $E_a = 93.3$ kJ mol⁻¹) can be attributed to the liberation energy of bulk water which fills the pores of the calcified matrix [1]. These values of E_a are much higher than values of E_a needed for the pure desorption of water molecules from the bone surface. The observed relatively wide range of the apparent activation energies (E_a) can be attributed to the existence of pore size distribution in the investigated bone samples [1]. Further increasing of α leads to the lowering the energy barrier (from $\alpha = 0.20$ to $\alpha = 0.70$), where the apparent activation energy value decreases. In

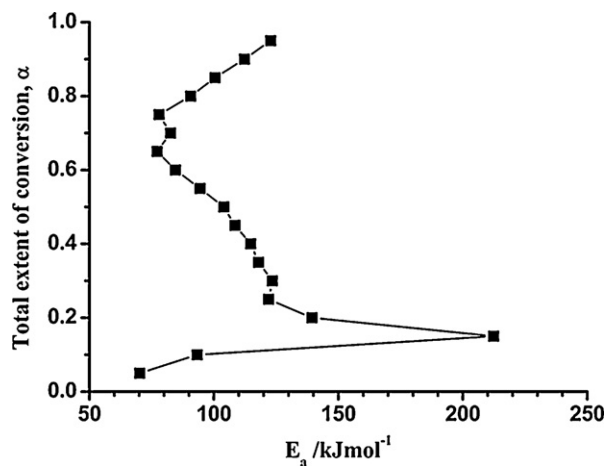


Fig. 7. The total extent of conversion (α) as a function of the apparent activation energy (E_a) derived from the Friedman's isoconversional method using the Weibull 3-mixture curve-fitting approach, for the bone combustion process in air atmosphere.

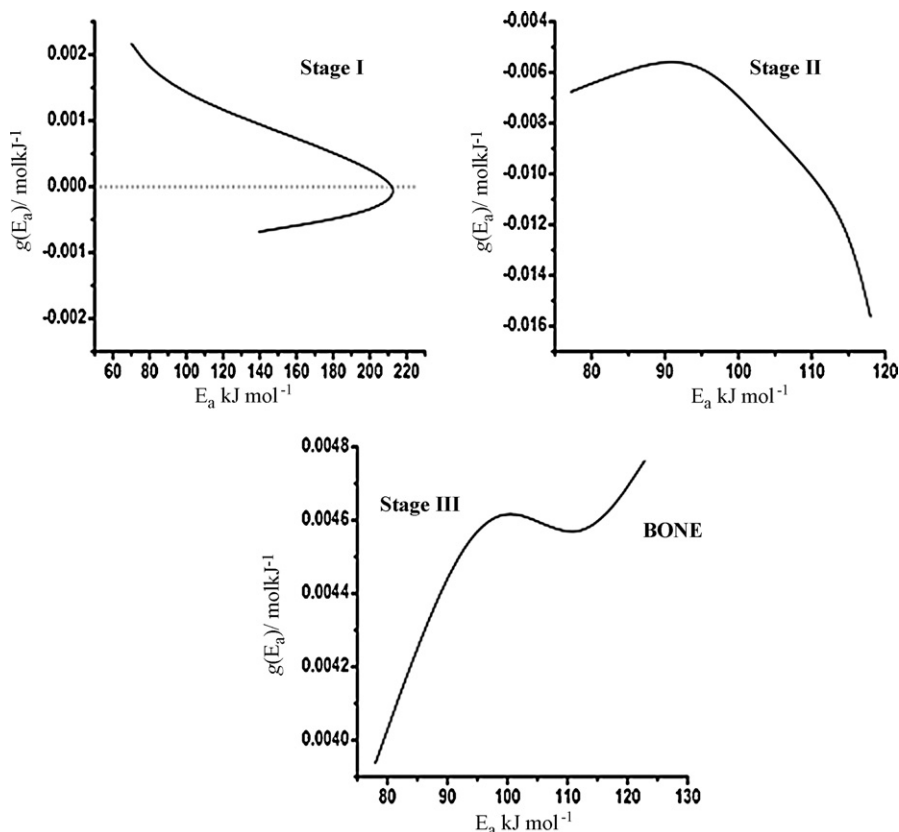


Fig. 8. Distribution function of the apparent activation energy ($g(E_a)$) for the first (I), second (II) and third (III) reaction stage of the bone combustion process.

this step, the degradation process of organic components (mainly collagen) is evident [1]. From $\alpha = 0.75$ up to $\alpha = 0.95$, the slightly higher energy barrier occurs, which lead to the increasing of the apparent activation energy value (Fig. 7).

Fig. 8 shows the distribution curves of the apparent activation energy values of the considered bone combustion process. As shown, they do not resemble a Gaussian curve proving the disadvantage of assuming 'a priori' forms for the $g(E_a)$ function.

It can be seen from Fig. 8, that the obtained $g(E_a)$ function for the first reaction stage exhibits asymmetrical behaviour with clearly defined maximum at $E_a = 212.4 \text{ kJ mol}^{-1}$ for $\alpha = 0.15$. From this result, it is evident that the first reaction stage cannot be approximated by the symmetrical bell-shaped Gaussian distribution. In addition, the distribution curve is denser for the higher values of the apparent activation energy (for $E_a > 120 \text{ kJ mol}^{-1}$ (Fig. 8)), which represents a result in the agreement with a heavier liberation of water molecules (see above discussion).

Finally, Fig. 8 compares the corresponding distribution curves for the second and third reaction stage of bone sample.

From the presented figure, we can observe that the shapes of distribution functions are significantly different, which indicates that the second and third reaction stage of investigated bone samples are governed by the different reaction mechanisms. The distribution function for the second reaction stage exhibits maximum at the exactly of $E_a = 94.5 \text{ kJ mol}^{-1}$ for $\alpha = 0.55$, while the distribution function for the third reaction stage exhibits maximum value at the exactly of $E_a = 100.5 \text{ kJ mol}^{-1}$ which corresponds to the conversion value of $\alpha = 0.85$. Namely, this behaviour is an evidence of multi-steps reactions and the consequently changing of the reaction mechanisms at the selected conversion range. The confirmation of these results using the conventional kinetic analysis is given in our previous paper [1]. Generally speaking, the established model gives a very good approximation of the temperature

range where the investigated combustion process will take place even now at the higher heating rates ($\nu_h = 20^\circ\text{C min}^{-1}$).

The main advantage of the proposed Weibull mixture model for modelling the kinetics of non-isothermal combustion process of animal bones is that the model can be determined by relatively few parameters. The shape parameter (β) should indicate the kinetic pattern of the process within a limited range of temperatures (referring to the individual reaction stages). The established distribution parameters in the considered Weibull mixture model, enable us that from the fitted data, we can evaluate some data required for the isoconversional kinetic analysis.

6. Conclusions

In this paper, we were applied the statistical method to optimize the fitting of the kinetic conversion data for animal bone combustion process, by the linear combination of the few Weibull distribution functions. The separation into single functions provides an approach to separate the different reaction stages, because every reaction stage was characterized by one Weibull distribution function with specific values of distribution parameters (β_i , η_i). The alterations of distribution parameters in the Weibull mixture models, indicates a probably change of the kinetic nature of the particular reaction stage.

A model with a continuous distribution of the apparent activation energy can adequately represent the individually stages of complex bone combustion process. From the characterization of the estimated distribution curves, we can bring some important conclusions about the kinetics of the considered bone combustion process.

The calculated distribution parameters in the Weibull mixture model, enable us that from the fitted data, we can evaluate some data required for the isoconversional kinetic analysis.

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