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KINETIC EQUATIONS FOR THERMAL DISSOCIATION PROCESSES
Part I. KEKAM equation

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Abstract

Relationships have been established between the average conversion degree and the dissociation time for polydisperse granular material, taking its grain size distribution into account. It has been checked in which cases the kinetic curves obtained by a numerical solution can be described in terms of KEKAM equation.

Keywords: KEKAM equation, kinetics, thermal dissociation of solids

Introduction

The general description of the macromechanism of thermal dissociation of solids by means of the well-known kinetic equations, is usually based on the single grain model [1–10]. If the reaction system contains W grains of identical initial size, then the kinetic equation should not change, because the transformation degree for W equal grains is calculated analogously to that for a single grain.

In the case of polydisperse systems (with different grain size) the transformation degree is different for grains with different initial dimensions and it can be described by the following relation:

$$\overline{\alpha} = 1 - \int_{R_i=0}^{R=R_m} [1 - \alpha(R_i)] f(R) \mathrm{d}R \tag{1}$$

where $\overline{\alpha}$ – mean value of transformation degree, $\alpha(R_i) \in <0;1>$, $\alpha(R_i)$ – transformation degree for grain fraction with initial radius R_i, $f(R)$ – density function for the grain size distribution, characteristic for polydisperse system, R_m – initial radius of the largest grains, present in the reaction system.

In the case of thermal dissociation of the type $A_{solid} \rightarrow B_{solid} + C_{gas}$, the rate of migration of the solid phase boundary: starting material –product (i.e. the zone of chemical reaction) in a single grain (or in the system of W identical grains) can be de-

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scribed by equations proposed by Huttig (also referred to as Spancer–Topley equation) or by Jander:

a) for the kinetic region (where the total rate of the process is limited by the rate of chemical reaction):

$$1-(1-\alpha)^{1/3}=\frac{k_1}{R_i}t \tag{2}$$

b) for the diffusion region (where the total rate of the process is limited by the diffusion rate in the layer of solid product formed on the grain of starting material):

$$[1-(1-\alpha)^{1/3}]^2=\frac{k_2}{R_i}t \tag{3}$$

where k_1, k_2 – rate constants for the kinetic and diffusion regions of the process, respectively; t – time elapsed from the start of decomposition.

Until now, the possibility of applying the kinetic Eqs (2) and (3) to the description of the process of thermal dissociation in the systems of non-uniform grain size has been checked for the cases of:

a) normal distribution, characteristic of mechanically or manually disintegrated material, for which the density function is described as follows:

$$f(R)=\frac{1}{\delta\sqrt{2\pi}}\exp\left[-\frac{1}{2}\left(\frac{R-\overline{R}}{\delta}\right)^2\right] \tag{4}$$

and the cumulative distribution function is given by the relationship:

$$F(R_z)=\sqrt{\frac{B}{\pi}}\int_{-\infty}^{R_z}\exp[-B(R_z-1)^2]\mathrm{d}R_z \tag{5}$$

In this equations: δ – variance, $\overline{R}$ – mean grain radius, $B=\overline{R}/2\delta^2$, $R_z=R/\overline{R}$

b) the Rosin–Rammler–Sperling distribution, characteristic of materials obtained by crystallisation, for which the density function is described as follows :

$$\varphi(R)=n\left(\frac{1}{R}\right)^n R^{n-1}\exp\left[-\left(\frac{R}{\overline{R}}\right)^n\right] \tag{6}$$

and the distribution function assumes the form:

$$\Phi(R)=1-\exp(-R_z^n) \tag{7}$$

where n – parameter, characteristic of grain size distribution, the value of n can be determined from the relationship between log log($1/y$) and log$R$ (y is weight fraction of grains of $R>R_i$).

A dimensionless variable $R_z=R/\overline{R}$ has been introduced to the kinetic Eqs (2) and (3) and maximum transformation time ($t_{m,i}$) has been calculated for the fraction of radius R_i. For the kinetic range we have obtained:

$$t_{m,i}=\frac{R_i}{k_{1,i}}=\frac{R_{z,i}\overline{R}}{k_{1,i}} \tag{8}$$

and for the diffusion region:

$$t_{m,i}=\frac{R_i^2}{k_{2,i}}=\frac{R_{z,i}^2\overline{R}^2}{k_{2,i}} \tag{9}$$

For the kinetic region it has been determined:

$$\theta_{k,i}=\frac{k_{1,i}t_{m,i}}{\overline{R}}=R_{z,i} \tag{10}$$

and for the diffusion region

$$\theta_{d,i}=\frac{k_{2,i}t_{m,i}}{\overline{R}^2}=R_{z,i}^2 \tag{11}$$

After having introduced the relationships (8) and (10), as well as (9) and (11) to the kinetic Eqs (2) and (3) it has been found that, these equations are identical. Therefore, it has become possible to take into account only two Eqs, (12) and (13), for which the distribution function and the relation $dR=\overline{R}dR_z=\overline{R}d\theta$ for the normal (12) and Rosin–Rammler–Sperling (13) distribution, respectively:

$$\overline{\alpha}=1-\left\{\sqrt{\frac{B}{\pi}}\int_{\theta_1}^{\theta_m}\left(1-\frac{\theta_1}{\theta}\right)^3\exp[-B(\theta-1)^2 d\theta\right\} \tag{12}$$

$$\overline{\alpha}=1-\left\{n\int_{\theta_1}^{\theta_m}\left(1-\frac{\theta_1}{\theta}\right)^3\theta^{n-1}\exp[-\theta^n]d\theta\right\} \tag{13}$$

From Eq. (12) the values of $\overline{\alpha}$ have been calculated for $B=\in<0.01; 1000>$ and for $\theta\in<0.001; 2>$. The kinetic curves obtained were treated by means of Eqs (2) and (3). The value of $\overline{\alpha}$ from Eq. (13) was calculated for $n=n\in<1.00; 3.00>$ and for $\theta\in<0.001; 2>$. The kinetic curves obtained were described by Eqs (2) and (3).

The calculations have shown, that in the case of normal distribution the thermal dissociation of polydisperse material can be described only by means of Eq. (2) and only for the values of $B\geq 20$, whereas in the case of the Rosin–Rammler–Sperling distribution only Eq. (3) was applicable and only for $n=1$, and for n slightly greater than 1.

The description of the kinetics by means of Eq. (2) with the condition:

$$B=\frac{\overline{R}^2}{2\delta^2}\geq 20 \tag{14}$$

shows, that for $\overline{R}$=1 the mean deviation may not exceed the value 0.158 ($\delta \leq 0.158$).

The mathematical description of the process under consideration, by means of Eq. (2), becomes possible only in cases where R fulfils the condition $R \in <0.5;\ 1.5>$ i.e. when the range of variation of R is comparatively small.

In the cases where the grain size distribution is of the Rosin–Rammler–Sperling type the nature of the decomposition depends on the value of n, and for every value of n the distribution function and the density function may assume various forms [1].

The mathematical description of thermal dissociation of polydisperse material by means of Eq. (3) is possible in quite a large range of variability of R (($R/\overline{R} \in <0;\ 4>$), if n=1 or slightly exceeds the value of 1, i.e. where the Rosin–Rammler–Sperling distribution is similar to the exponential distribution.

The results of the calculations have shown that the type and the nature of grain size distribution of a polydisperse reacting material should be taken into account in the analysis of kinetic data, since it determines the possibility of their mathematical processing.

Formulation of the problem

The aim of the first stage of this work was check the possibility of using other kinetic equations for describing the process of thermal dissociation occurring in the polydisperse system.

We have started with the following equation :

$$-\ln(1-\alpha)=kt^{\mathrm{n}} \tag{15}$$

sometimes referred as Avrami–Erofeev (AE) or KEKAM (Kazaev–Erofeev–Kołmogarov–Avrami–Mampel) equation (F1).

Equation (15) has been used for the description of many reactions of thermal dissociation. Although it has been derived with assumption, that the process of thermal dissociation of the type $A_{\mathrm{solid}} \rightarrow B_{\mathrm{solid}} + C_{\mathrm{gas}}$ is controlled by the rate of nucleation of the new phase and migration of the substrate – product boundary due to the growth of the nuclei, its great advantage is the very good description of the kinetic curves of the topochemical processes at different values of n. So, e.g. for n=1 Eq. (15) describes very well the kinetic curves of 1st order reactions, for n=0.63 – the kinetic curves characteristic of 2nd order reactions, and of n=0.5 – reactions in the diffusion region.

The possibility of using KEKAM equation for mathematical description of the process of thermal dissociation of polydisperse substances has been checked for the systems, in which the grain size is described in terms of the normal and Rosin–Rammler–Sperling equations, i.e. where the grain size distribution density functions are given by Eqs (4) and (6), and the distribution functions by Eqs (5) and (7), respectively.

A dimensionless variable $R_z=R/\overline{R}$ is introduced into Eq. (4) and the maximum time of transformation of the fraction R_i is calculated. The equation loses its physical sense for α=1, hence α=0.99 has been accepted for $t_{\mathrm{m,i}}$.

Assuming, that n=1 Eq. (15) accepts the form:

$$-\ln(1-\alpha)=kt \tag{16}$$

taking $k=k_i/R_i$ we obtain for a fraction of radius R_i:

$$-\ln(1-\alpha)=\frac{k_i t_i}{R_i} \tag{17}$$

hence, for a fraction of radius R_i and $\alpha=0.99$ we obtain:

$$t_{m,i}=4.6\frac{R_i}{k_i} \tag{18}$$

the relation $k_i t_{m,i}=4.61R_i$ may be regarded as dimensionless variable θ, hence:

$$\theta=k_i t_{m,i}=R_{z,i} \tag{19}$$

Assuming, that $\bar{R}=1$ the transformation degree $\alpha(R_i)$ for selected fractions and known maximum time $t_{m,i}$ can be checked with the use of Eq. (16).

Transformation of the Eq. (16) for a fraction of radius R_i gives:

$$\alpha(R_i)=1-e^{-k_i t_{m,i}/R_i} \tag{20}$$

and from relation (18) we obtain:

$$\alpha=1-e^{-4.61} \tag{21}$$

hence $\alpha=1-0.01=0.99$ in conformity with the assumption.

If we put in Eq. (1) the transformed relationship (16) and the density function $f(R)$ for the normal distribution, and when $dR=\bar{R}dR_z=\bar{R}d\theta$, we obtain:

$$\bar{\alpha}=1-\left\{\frac{1}{\delta\sqrt{2\pi}}\int_{R=0}^{R=R_m}[1-\alpha(R_i)]\exp\left[-\frac{1}{2}\left(R-\frac{\bar{R}}{\delta}\right)^2\right]dR\right\} \tag{22}$$

Since $\theta=k_i t_{m,i}$ we have:

$$\alpha(R_i)=1-e^{-\theta} \tag{23}$$

then

$$\bar{\alpha}=1-\left\{\frac{1}{\delta\sqrt{2\pi}}\int_{\theta_1}^{\theta_m}\left[1-(1-e^{-\theta})\exp\left[-\frac{1}{2}\left(R-\frac{1}{\delta}\right)^2\right]\right]d\theta\right\} \tag{24}$$

Equation (24) comprises the terms: $1/\delta\sqrt{2\pi}$ and $-1/2[(R-1)/\delta]^2$. We insert a dimensionless variable $B=1/2\delta^2$ to the former of them with assumption $\bar{R}=1$. Then $\delta^2=1/2B$ hence:

$$\delta=\sqrt{\frac{1}{2B}} \tag{25}$$

The other expression is transformed into the following form, taking into account the value of δ^2 and Eq. (19):

$$-\frac{1}{2}\frac{(R-1)^2}{\delta^2}=-\frac{1}{2}\left(\frac{(R-1)^2}{\frac{1}{2B}}\right)=[-B(\theta-1)^2] \tag{26}$$

Introducing the relationships (25) and (26) into (24) gives the following expression for $\overline{\alpha}$ in the normal distribution :

$$\overline{\alpha}=1-\left\{\sqrt{\frac{B}{\pi}}\int_{\theta_1}^{\theta_m}\mathrm{e}^{-\theta_i}\exp[-B(\theta-1)^2]\mathrm{d}\theta\right\} \tag{27}$$

An analogous solution applied for the case of Rosin–Rammler–Sperling distribution, under identical assumptions, gives the following relation:

$$\overline{\alpha}=1-\left[n\int_{\theta_1}^{\theta_m}\mathrm{e}^{-\theta_i}\theta^{n-1}\exp(-\theta^n)\mathrm{d}\theta\right] \tag{28}$$

Calculation results and discussion

1. The *Turbo Pascal 6.0* language has been applied for developing the program *Kinet 1* (Annex 1) which enables:

a) calculation of the values of α for $B\in<0.001;\ 1000>$ at $\theta\in<0.001;\ 2>$ by means of Eq. (27);

b) finding the kinetic curves of the function $\overline{\alpha}=f(\theta)$ for any values of B described as above. The process of finding the kinetic curves $\overline{\alpha}=f(\theta)$ consists in entering successive values of B and $\theta\in<0.001;\ 2>$; to the program which calculates the kinetic curves and displays its image on the screen. After appropriate scanning of B values in the range $B\in<1;\ 22>$ it has become possible to find those values for which the kinetic curves begin at the origin. These were the values in the range $B\in<3;\ 7>$. The results of calculations of $\overline{\alpha}=f(\theta)$ are shown in Figs 1a and 1b.

The procedure has been applied using Eq. (27) for the normal distribution.

2. A similar procedure was also applied for deriving the kinetic curves for the Rosin–Rammler–Sperling distribution with the use of Eq. (28). In this case the values of n and θ were entered into the computer program using the values of $n\in<0.001;\ 4>$ and $\theta\in<0.001;\ 2>$. From among all kinetic curves of $\overline{\alpha}=f(\theta)$ only those were taken into account, which had their beginning in the origin of the co-ordinate system, i.e. where $n\in<0.03;\ 0.09>$. The results of the calculations are shown in Fig. 2.

Only those kinetic curves, that begin in the origin of co-ordinate system have been utilised for further processing. In the case of normal distribution they were the curves obtained for B=3, 4, 5, 6, 7, and for the Rosin–Rammler–Sperling – the curves

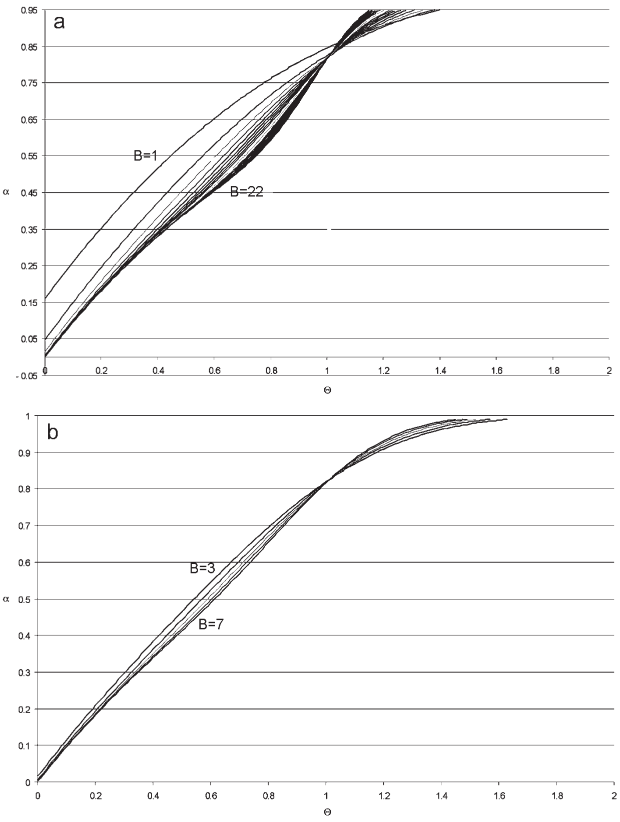

Fig. 1 Kinetic curves: a – for $B\in<1; 22>$, b – for $B\in<3; 7>$

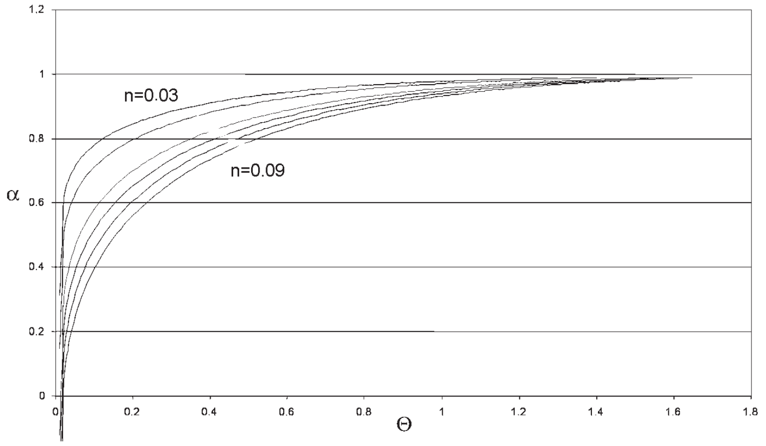

Fig. 2 Kinetic curves of Rosin–Rammler–Sperling distribution for $n\in<0.03; 0.09>$

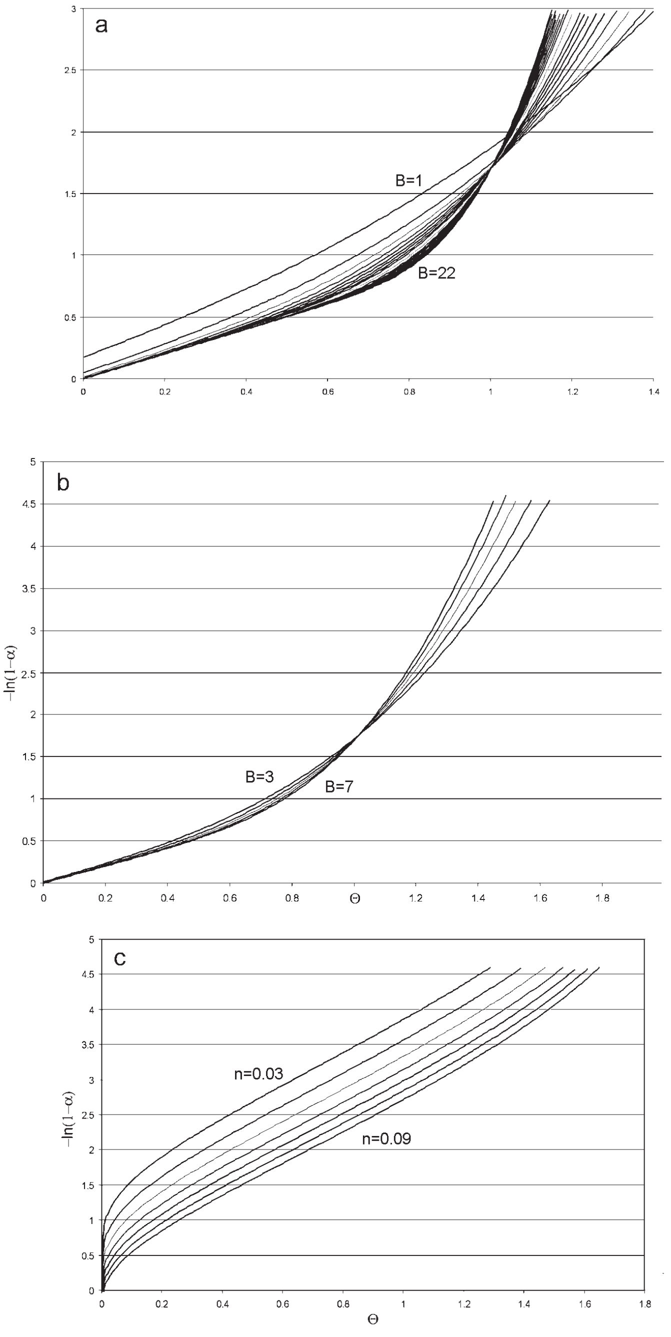

Fig. 3 Kinetic curves calculated from Eq. (16): a – for $B\in<1; 22>$; b – for $B\in<3; 7>$, c – for Rosin–Rammler–Sperling distribution

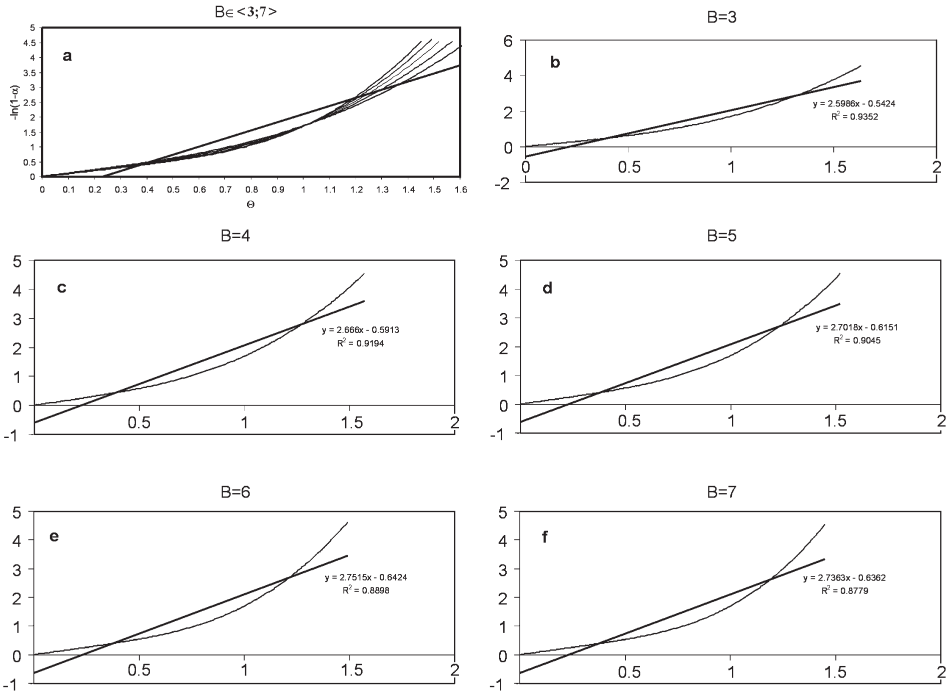

Fig. 4 Approximation of curves for normal distribution: a – total approximation, b–f – individual approximation

obtained for $n=n\in<0.03;\ 0.09>$. The results are shown in Fig. 3a and 3b (for the normal distribution), and Fig. 3c (for the Rosin–Rammler–Sperling distribution).

The possibility of using Eq. (16) for the description of thimble dissociation of polydisperse solids has been checked by the linear approximation of the curves obtained for the normal distribution and for selected values of B with the aim of establishing which ranges of the kinetic curve can be described in terms of that equation. Joint approximation of all the curves selected (Fig. 4a) and approximation of single curves (Fig. 4b, 4c, 4d, 4e, 4f) failed because of the very large value of variance and small regression.

For that reason attempt has been made to carry out the stepwise approximation of selected sections of the curves.

In the first step the curves obtained for B=3; 4; 5; 6 and 7 were divided into two sections from $\theta_1=0.01$ to $\theta_2=0.8006$ and from $\theta_3=1.18041$ to $\theta_4=1.630185$. The values of regression r^2 and variance δ were calculated for each section of all the curves (Fig. 5).

In the second step the middle section of all the curves approximated from $\theta_2=0.8006$ to $\theta_3=1.18041$ and the values of regression and variance were determined. The results are shown in Fig. 5.

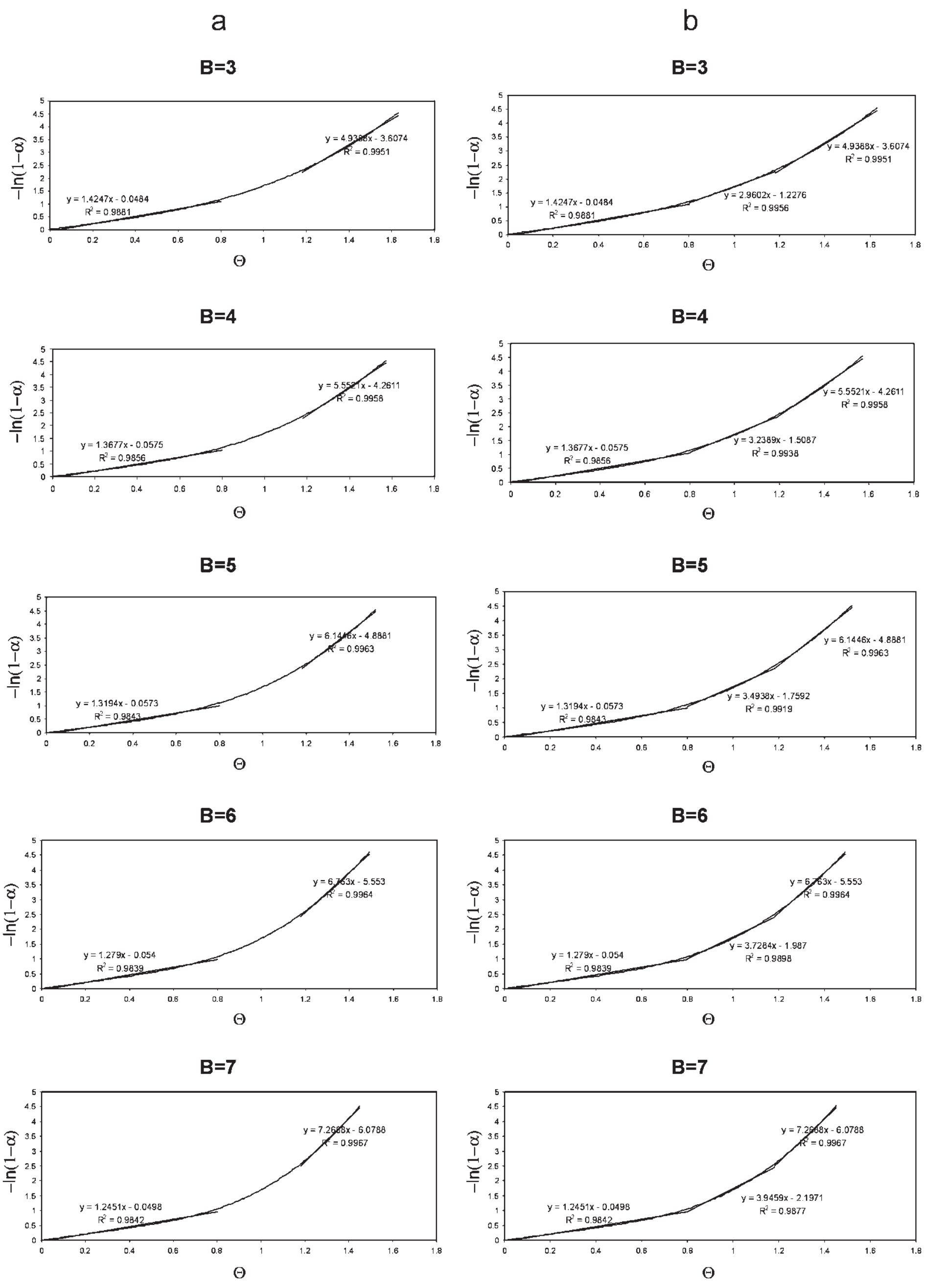

Fig. 5 Approximation of curves by sections: a – for two sections, b – for three sections

Table 1 The results of calculations

	Normal distribution				
The values of B	B=3	B=4	B=5	B=6	B=7
The boundary of changing of $(\bar{\alpha})$ for Eq. (27)	0.01585–0.984	0.0059–0.989	0.0027–0.9893	0.00157–0.989	0.0012–0.989
The boundary of changing of $-\ln(1-\alpha)$	0.016–1.186 1.186–2.313 2.313–4.547	0.0059–1.142 1.142–2.380 2.380–4.546	0.0027–1.1085 1.1085–2.441 2.441–4.5328	0.0157–1.082 1.082–2.320 2.320–4.6036	0.0012–1.059 1.059–2.346 2.346–4.531
The boundary of changing of (α) for Eq. (16)	0.01585–0.695 0.695–0.9011 0.9011–0.989	0.0059–0.682 0.682–0.9071 0.9071–0.989	0.0027–0.669 0.669–0.9139 0.9139–0.989	0.00157–0.669 0.669–0.91838 0.91838–0.989	0.0012–0.662 0.662–0.9233 0.9233–0.989
Variance (δ) at total approximation	0.01071742	0.01431362	0.01724538	0.0204185	0.02170669
Regression	0.9352	0.9194	0.9045	0.8898	0.8779
The variance of curves at approximation by sections	0.000359921 0.0000111945 0.000003118	0.000408832 0.00001965 0.000002317	0.00041375 0.000030582 0.000001785	0.00039424 0.000044112 0.000001551	0.00036125 0.0041334 0.000001162
Regression	0.9881 0.9956 0.9951	0.9856 0.9938 0.9958	0.9843 0.9919 0.9963	0.9839 0.9898 0.9964	0.842 0.9877 0.9967
The boundary of changing of $(\bar{\alpha})$ at finding the logarithm	0.01585–0.901 0.901–0.989	0.0059–0.907 0.907–0.989	0.0027–0.9139 0.9139–0.989	0.00157–0.918 0.918–0.989	0.0012–0.9233 0.9233–0.989
Regression at finding the logarithm	0.998	0.9942	0.9894	0.984	0.9786
Regression of the logarithmed section	0.9983	0.9985	0.9988	0.9991	0.9993

	Rosin–Rammler–Sperling distribution						
The values of n	0.030	0.04	0.05	0.06	0.07	0.08	0.09
The boundary of changing of $(\bar{\alpha})$	0.841511 0.989923	0.753283 0.989785	0.695259 0.989894	0.638520 0.989939	0.583014 0.989664	0.528642 0.989699	0.475346 0.989975
Regression	0.9996	0.9994	0.9991	0.9987	0.9983	0.9976	0.9968

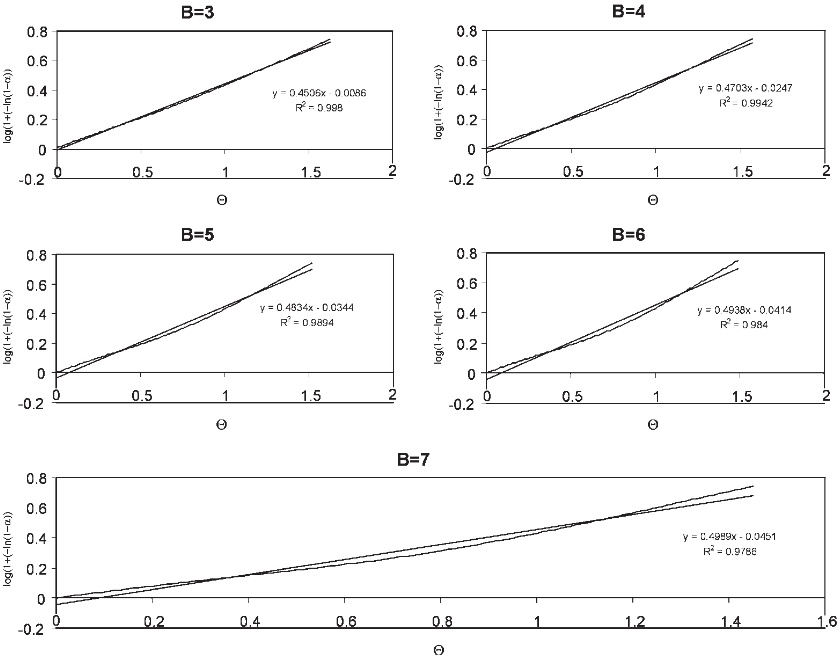

Fig. 6 Total finding the logarithm for curves of normal distribution

The difficulties connected with interpretation of the curves divided into three sections have led to a necessity of searching for another solution of the problem. After having studied many possibilities it has been found that taking the logarithm of Eq. (16) may lead to an acceptable solution, since it enables to get a linear approximation of the straight lines, for selected values of B after addition of a certain constant in order to shift the scale of the diagram. Such a procedure has made it possible to obtain ideal straight lines for the values of $B=3$ and $B=4$, and an approximation very close to straight lines, for $B=5$, $B=6$ and $B=7$. The results are shown in Fig. 6.

The first section of the curve between $\theta_1=0.001$ and $\theta_2=0.8006$ is a straight line. For this reason only for the approximation of the second section of the curves between $\theta_2=0.8006$ and $\theta_4=1.630185$ it was necessary to logarithm the Eq. (16). The result of this action, in the form of a straight line, is shown in Fig. 7. The variance and the mean deviation have been calculated with the air of $\overline{\alpha}$. The calculations have been made for $\alpha\in<0.016; 0.99>$.

The values of $\overline{\alpha}$ from Eq. (28) for the Rosin–Rammler–Sperling distribution have been determined with the aid of program (Kinet 2), also using the language Turbo Pascal 6.0 (Annex 2). The calculations were carried out for the values of $n\in<0.01; 4>$ and for $\theta\in<0.001; 2>$. The kinetic curves obtained $n=n\in<0.03; 0.09>$, are shown in Fig. 2. Equation (16) has been used for further processing of the results. The curves $-\ln(1-\alpha)=f(\theta)$ obtained for selected values of n are shown in Fig. 3c.

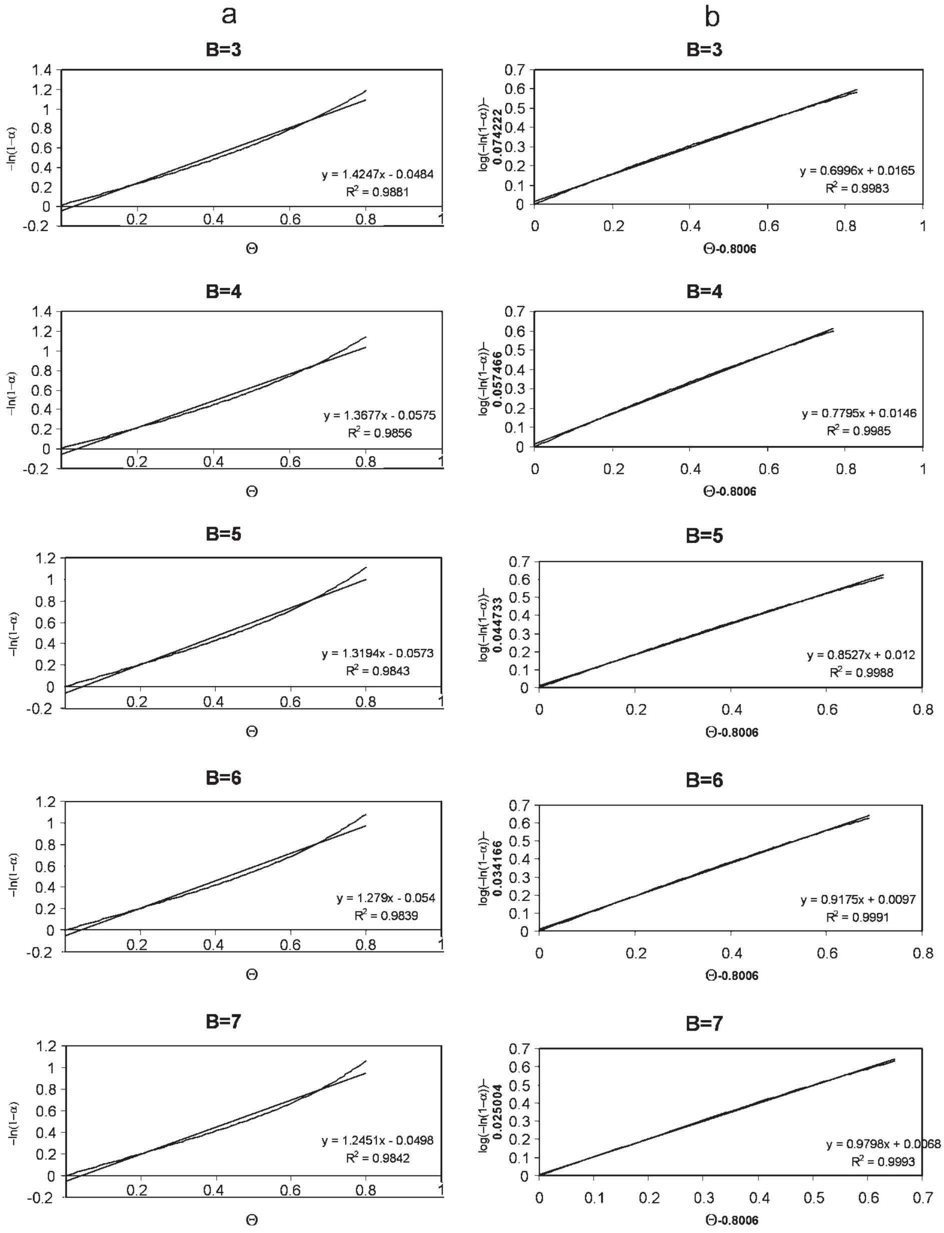

Fig. 7 Linear approximation for: a – first section of curves, b – second logarithmed section

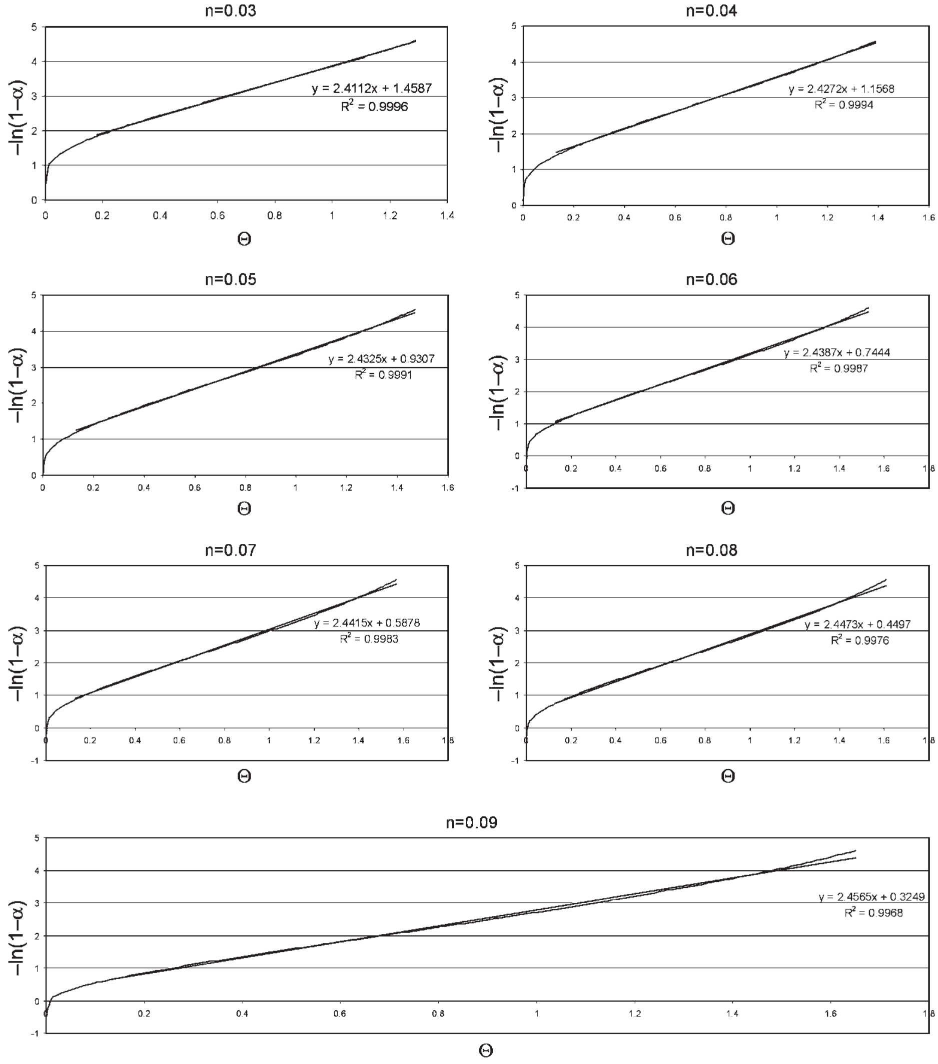

Fig. 8 Approximation of curves of Rosin–Rammler–Sperling distribution

Linear approximation of the curves obtained for each value of n has been shown in Fig. 8. The calculations have shown that in the case of normal distribution of grain size the process of thermal dissociation of polydisperse material can be described by Eq. (16) for B=3, 4, 5, 6, and 7 only in individual sections (see data of Fig. 7 and data from the Table). Equation (16) describes the process of thermal dissociation of polydisperse material in the case of Rosin–Rammler–Sperling for n=n∈<0.03; 0.09>. The results are shown in Fig. 8.

The determination of the value of $\overline{R}$ made it possible to calculate the value of distribution function and density function for $\overline{R}$=1; R∈<0.5; 1.5> in normal distribution.

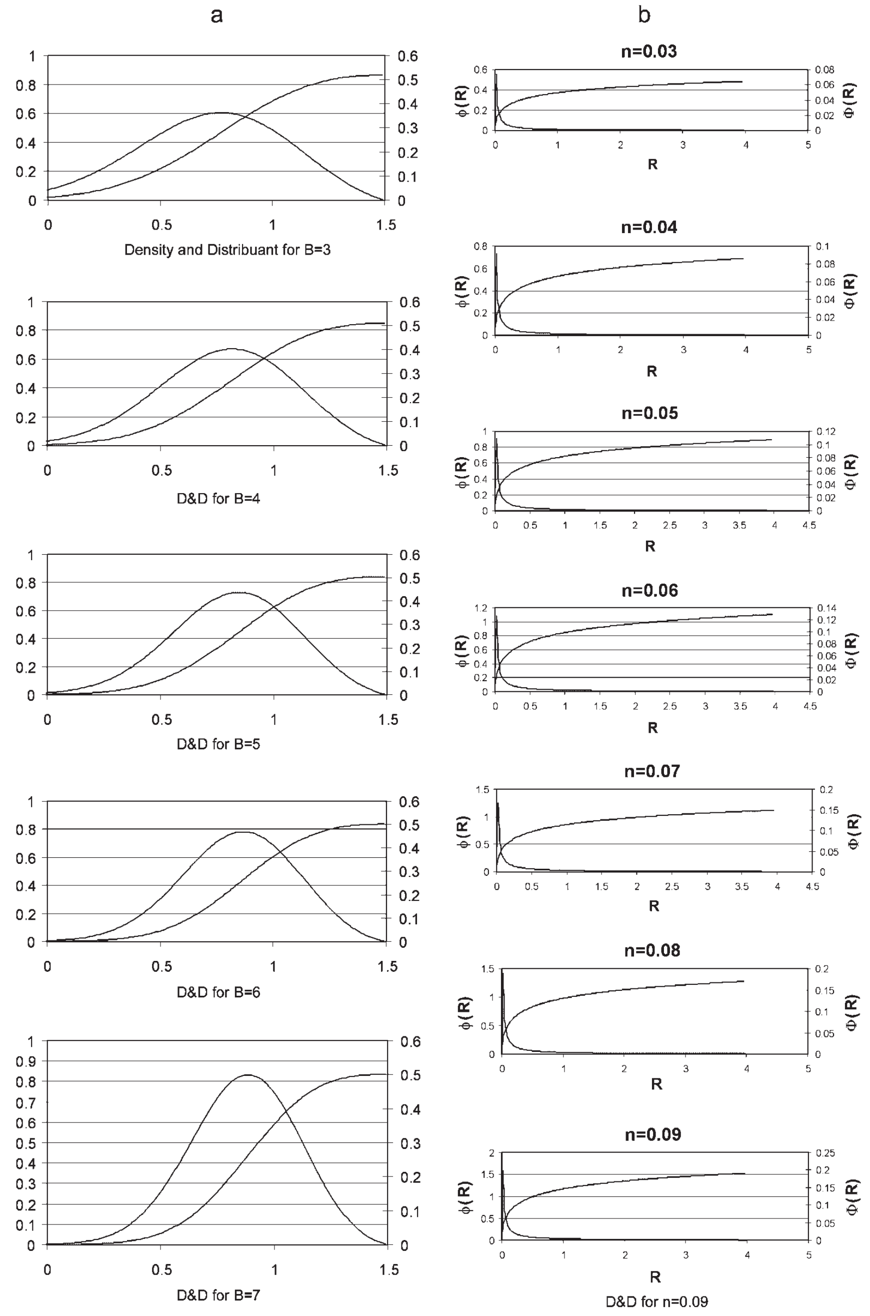

Fig. 9 Density functions and distribuants: a – for normal distribution, b – for Rosin–Rammler–Sperling distribution

The values of mean deviation have also been calculated for selected values of

$$B=\frac{\overline{R}^{2}}{2\delta^{2}}\ \text{for}\ \overline{R}=1.$$

B	3	4	5	6	7
δ	0.408	0.354	0.316	0.289	0.267

For $\overline{R}=1$ the mean deviation can not exceed 0.408 ($\delta=0.408$). The results of calculation of the density function and distribution function are represented in Fig. 9a.

In the case of polydisperse material with Rosin–Rammler–Sperling distribution the character of distribution only slightly depends on the value of n; the values of distribution function and density function have been calculated for different n values by means of Eqs (6) and (7), for $R\in<0;\ 4.5>$. They are shown in Fig 9b.

Conclusions

Mathematical description of the process of thermal dissociation of polydisperse material with normal distribution of grain size is possible with the use of Eq. (16), if $R\in<0.5;\ 1.5>$, i.e. for narrow range of R. On the other hand, in the case of Rosin– Rammler–Sperling distribution much wider range of R is admissible, namely $R\in<0;\ 4.5>$, but only for very small values of n which means, that the use of that equation for this type of grain size distribution is admissible only for very small ranges of variability of $\overline{\alpha}$.

Symbols

k	[mm s^{-1}]
B	[mm^2]
R, $\overline{R}$	[mm]
R_z, θ	[–]

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