

KINETIC EQUATIONS FOR THERMAL DISSOCIATION PROCESSES

Part III. Equations D1, F2 and F3

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Abstract

Relationships between average degree of transformation and time of dissociation were derived for polydisperse granular materials with account to the type of grain size distribution. It has been checked, under what conditions the kinetic curves obtained by numeric solution of those relationships may be described in terms of equations D1 $\alpha^2 = kt^{1/2}$, F2 $[1/(1-\alpha) - 1 = kt]$ and F3 $[1/(1-\alpha)^2 - 1 = kt]$

Keywords: kinetics in polydisperse systems, thermal dissociation of solids

Introduction

In foregoing parts of this work [1–3] we have presented a description of macro-mechanism of thermal dissociation of solids in terms of known kinetic equations for polydisperse system (of different grain size), in which the degree of transformation is different for grains differing in initial dimensions (R_i). The degree of transformation may be given by the following relationship:

$$\bar{\alpha} = 1 - \int_{R_i=0}^{R=R_m} [1 - \alpha(R_i)] f(R) dR \quad (1)$$

where $\bar{\alpha}$ – mean value of transformation degree, if $0 < (R_i) < 1$,
 $\alpha(R_i)$ – transformation degree of grain fraction of initial grain radius R_i ,
 $f(R)$ – density function for grain size distribution characterizing a polydisperse system,
 R_m – final radius of the coarsest grains present in the reaction system.

The aim of this part of the work was to check the possibility of using other kinetic equations for describing the process of thermal dissociation of solids occurring in polydisperse systems.

First we have used equation D1:

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$$\alpha^2 = kt^{1/2} \quad (2)$$

which describes the effect of diffusion of gaseous reaction product on the rate of thermal decomposition.

Equation (2) has been used for description of many thermal dissociation reactions proceeding in the diffusion region (where the overall reaction rate is limited by the rate of diffusion in the layer of solid product formed on the surface of the solid grain). This equation has been derived with assumption, often confirmed in practice, that the molar volume of the product is different from that of the starting material.

Another equation referred as F2 has the form:

$$[1/(1-\alpha)-1=kt] \quad (3)$$

is an equation of second order.

Equation F3

$$[1/(1-\alpha)^2-1=kt] \quad (4)$$

is a third-order equation.

The possibility of using the equations D1, F2, and F3 for mathematical description of thermal dissociation of polydisperse solids was checked for systems, in which the grain size is described by normal and Rosin–Rammler–Sperling distributions, i.e. for cases where the grain size distribution functions are given by the following equations:

$$f_N(R) = \frac{1}{\delta\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{R-\bar{R}}{\delta}\right)^2\right] \quad (5)$$

$$\varphi_R(R) = n\left(\frac{1}{R}\right)^n R^{n-1} \exp\left[-\left(\frac{R}{\bar{R}}\right)^n\right] \quad (6)$$

and the distribution functions have the form of the following relationships:

$$F_N(R) = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{R_z} \exp[-B(R_z-1)^2] dR_z \quad (7)$$

$$\Phi_R(R) = 1 - \exp(-R_z^n) \quad (8)$$

In the above equations:

δ – variance, \bar{R} – mean grain radius, $B = \bar{R}/2\delta^2$ and $R_z = R/\bar{R}$.

Problem laying down

A dimensionless variable $R_z = R/\bar{R}$ is inserted into the Eqs (2), (3) and (4) and the maximum time of conversion is calculated for the fraction of radius R_i . It follows from Eq. (2), that the maximum time of conversion of the i -th fraction for $\alpha=1$ is $t_{m,i}$. As for $\alpha=1$ Eqs F2 and F3 lose their physical meaning, the value of $\alpha=0.99$ should be assumed.

Assuming $k = k_i/R_i$ one obtains for a fraction of radius R_i for $\alpha=1$:

$$t_{m,i} = \frac{R_i}{k_i} = \frac{R_{z,i} \bar{R}}{k_i} \tag{9}$$

hence:

$$\theta_{k,i} = \frac{k_i t_{m,i}}{\bar{R}} = R_{z,i} \tag{10}$$

A density function $f(R)$ is introduced to the equation of mean transformation degree for normal distribution and it is assumed that $dR = \bar{R} dR_z = \bar{R} \cdot d\theta$; hence:

$$\bar{\alpha} = 1 - \left\{ \int_{R=0}^{R=R_m} [1 - \alpha(R_i)] \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{R - \bar{R}}{\delta} \right)^2 \right] dR \right\} \tag{11}$$

Assuming $\bar{R}=1$ we have $\theta_{k,i} = k_i t_{m,i}$ and the Eqs (2), (3) and (4) have the following forms:

a) $\alpha(R_i) = \sqrt{\theta} \tag{12}$

b) $\alpha(R_i) = 1 - \frac{1}{\theta + 1} \tag{13}$

c) $\alpha(R_i) = 1 - \frac{1}{\sqrt{\theta + 1}} \tag{14}$

Inserting the expressions (12), (13) and (14) into the Eq. (11) one obtains:

a) for Eq. D1:

$$\bar{\alpha} = 1 - \left\{ \int_{\theta_1}^{\theta_m} (1 - \sqrt{\theta}) \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{R - 1}{\delta} \right)^2 \right] d\theta \right\} \tag{15}$$

b) for Eq. F2:

$$\bar{\alpha} = 1 - \left\{ \int_{\theta_1}^{\theta_m} \left[1 - \frac{1}{\theta + 1} \right] \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{R - 1}{\delta} \right)^2 \right] d\theta \right\} \tag{16}$$

c) for Eq. F3:

$$\bar{\alpha} = 1 - \left\{ \int_{\theta_1}^{\theta_m} \left[1 - \frac{1}{\sqrt{\theta + 1}} \right] \frac{1}{\delta \sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{R - 1}{\delta} \right)^2 \right] d\theta \right\} \tag{17}$$

Equation (11) comprises the expressions $\frac{1}{\delta\sqrt{2\pi}}$ and $-\frac{1}{2}\left(\frac{R-1}{\delta}\right)^2$. We can insert a dimensionless variable $B = \frac{1}{2\delta^2}$ to the former and assume $\bar{R}=1$.

Hence:
$$\delta = \sqrt{\frac{1}{2B}} \quad (18)$$

For δ^2 the other expression may be converted into the following form

$$-\frac{1}{2} \frac{(R-1)^2}{\delta^2} = -\frac{1}{2} \left(\frac{(R-1)^2}{\frac{1}{2B}} \right) = -B(\theta-1)^2 \quad (19)$$

On inserting the relations (18) and (19) into the Eqs (15), (16) and (17) for $dR = \bar{R} \cdot dR_z = \bar{R}\theta$ one obtains the following relationship for Eq. D1 and normal distribution:

$$\bar{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} (1 - \sqrt{\theta_1}) \exp[-B(\theta-1)^2] d\theta \right\} \quad (20)$$

and for Rosin–Rammler–Sperling distribution:

$$\bar{\alpha} = 1 - \left\{ n \int_{\theta_1}^{\theta} (1 - \sqrt{\theta_1}) \theta^{n-1} \exp[-\theta^n] d\theta \right\} \quad (21)$$

For Eq. F2 and normal distribution it has the form:

$$\bar{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} \left(\frac{1}{\theta_1+1} \right) \exp[-B(\theta-1)^2] d\theta \right\} \quad (22)$$

and for Rosin–Rammler–Sperling distribution:

$$\bar{\alpha} = 1 - \left\{ n \int_{\theta_1}^{\theta} \left(\frac{1}{\theta_1+1} \right) \theta^{n-1} \exp[-\theta^n] d\theta \right\} \quad (23)$$

Equation F3 gives, at identical assumptions and analogous treatment, the following relationship for normal distribution:

$$\bar{\alpha} = 1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} \left(\frac{1}{\sqrt{\theta_1+1}} \right) \exp[-B(\theta-1)^2] d\theta \right\} \quad (24)$$

and the following form for Rosin–Rammler–Sperling distribution:

$$\bar{\alpha} = 1 - \left\{ n \int_{\theta_1}^{\theta} \left(\frac{1}{\sqrt{\theta_1+1}} \right) \theta^{n-1} \exp[-\theta^n] d\theta \right\} \quad (25)$$

Calculations

Equations (20)–(25) have no analytical solutions.

Numerical calculations in Turbo-Pascal language were carried out as follows: The calculations were performed for the values of B and θ for normal distribution and for n and θ for the case of Rosin-Rammler-Sperling distribution.

Equations (20), (22) and (24) were used for calculating the values of $\bar{\alpha}$ for $B \in \langle 0.001; 1000 \rangle$ and for $\theta \in \langle 0.001; 2 \rangle$.

After appropriate search among B values we have found those values for which the kinetic curves begin at the origin of coordinates.

Calculations performed for Eq. D1 enabled to find kinetic curves for normal distribution if $B \in \langle 0.75; 0.85 \rangle$; they have been described in terms of Eq. (2).

When using an analogous procedure we have found, for Eq. F2, kinetic curves for normal distribution if $B \in \langle 2; 9 \rangle$; they have been described in terms of Eq. (3).

The kinetic curves were obtained for Eq. F3 if $B \in \langle 4; 10 \rangle$ and normal distribution; they have been described in terms of Eq. (4). The results of calculations of kinetic curves described by Eqs (2)–(4) are shown in Figs 1a and 1b, 2a and 2b, and 3a and 3b.

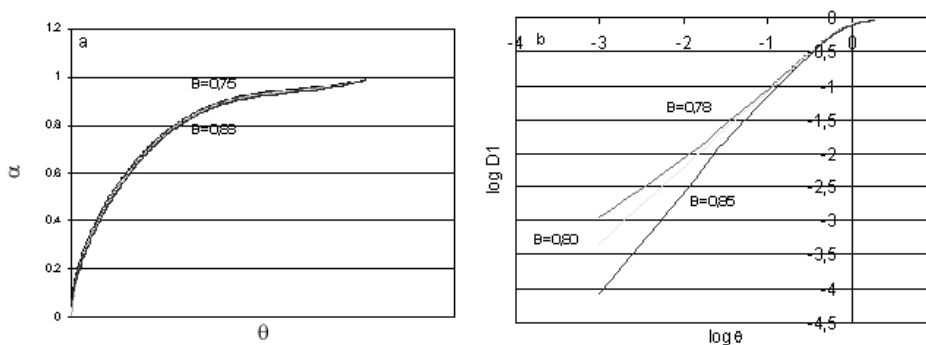


Fig. 1 Curves for Eq. D1: a – kinetic curves for $B \in \langle 0.75; 0.88 \rangle$, b – curves calculated from 2 for $B \in \langle 0.78; 0.85 \rangle$ in normal distribution

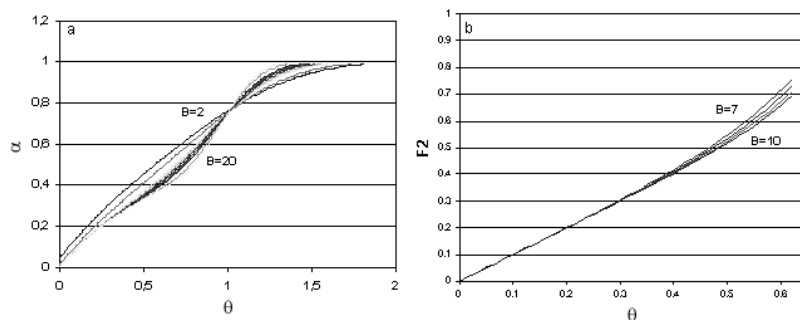


Fig. 2 Curves for Eq. F2: a – kinetic functions for $B \in \langle 2; 20 \rangle$, b – curves calculated from 3 for $B \in \langle 7; 10 \rangle$ in normal distribution

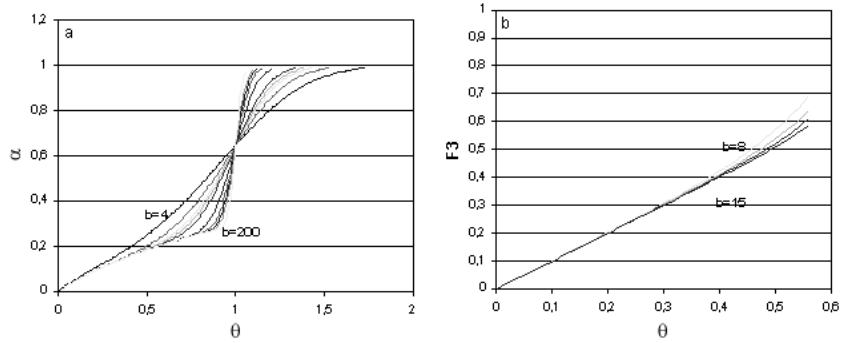


Fig. 3 Curves for Eq. F3: a – kinetic functions for $B \in \langle 4; 200 \rangle$, b – curves calculated from 4 for $B \in \langle 8; 15 \rangle$ in normal distribution

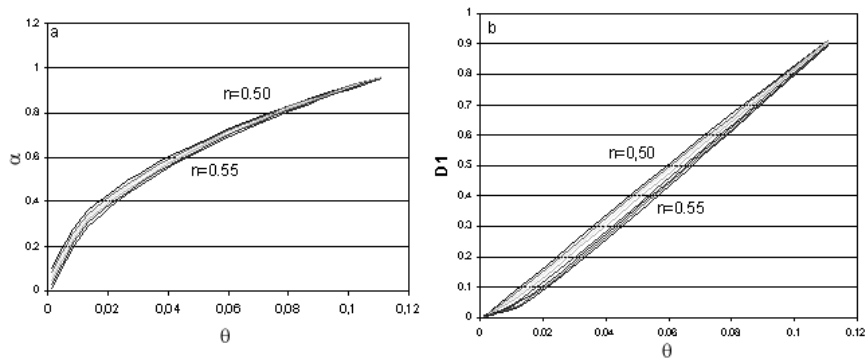


Fig. 4 Curves for Eq. D1: a – kinetic functions for $n \in \langle 0.45; 0.58 \rangle$, b – curves calculated from 2 for $B \in \langle 5; 0.58 \rangle$ in Rosin–Rammler–Sperling distribution

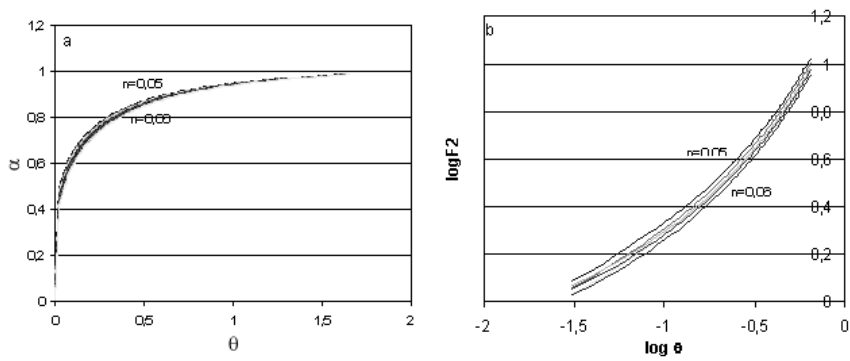


Fig. 5 Curves for Eq. F2: a – kinetic functions for $B \in \langle 0.40; 0.05 \rangle$, b – curves calculated from 3 for $B \in \langle 0.41; 0.046 \rangle$ in Rosin–Rammler–Sperling distribution (not applicable)

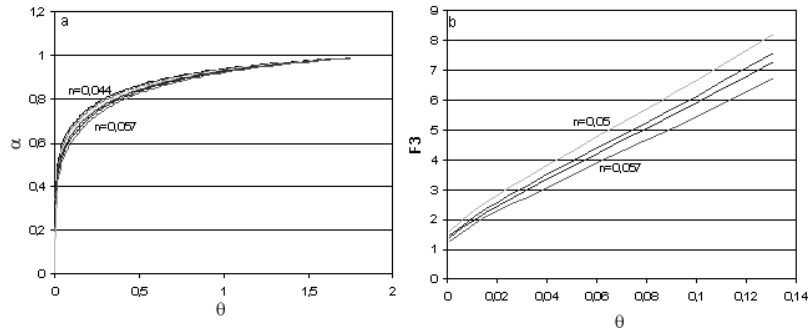


Fig. 6 Curves for Eq. F3: a – kinetic functions for $B \in \langle 0.040; 0.55 \rangle$, b – curves calculated from 4 for $B \in \langle 0.042; 0.049 \rangle$ in Rosin–Rammler–Sperling distribution (not applicable)

In an analogous procedure using Eqs (21), (23) and (25) we have calculated the values of $\bar{\alpha}$ for $n \in \langle 0.001; 1 \rangle$ and $\theta \in \langle 0.001; 2 \rangle$. After appropriate search among the values of n we have found those values of n , for which the kinetic curves have the start point at the coordinate origin. The curves were obtained:

- for Eq. D1 and Rosin–Rammler–Sperling distribution, if $n \in \langle 0.50; 0.55 \rangle$,
- for Eq. F2; it does not describe the kinetics in the Rosin–Rammler–Sperling distribution,
- for Eq. F3 it does not describe the kinetics in the Rosin–Rammler–Sperling distribution.

The kinetic curves have been described in terms of the Eqs (2), (3) and (4), and the results have been presented in Figs 4a and 4b, 5a and 5b, 6a and 6b.

Discussion of results

The description of the kinetics in terms of Eqs (2), (3) and (4) with the following conditions:

$$B = \frac{\bar{R}^2}{2\delta^2} \geq 0.78 \tag{26}$$

$$B = \frac{\bar{R}^2}{2\delta^2} \geq 7 \tag{27}$$

and
$$B = \frac{\bar{R}^2}{2\delta^2} \geq 8 \tag{28}$$

means, that for $\bar{R}=1$ the mean deviation can not exceed the value of 0.8006 ($\delta \leq 0.8006$) for Eq. D1, the value of 0.267 ($\delta \leq 0.267$) for Eq. F2, and the value of 0.25 ($\delta \leq 0.25$) for Eq. F3. Hence a mathematical description of the processes under discussion, in terms of Eqs (2), (3) and (4), is admissible for R values within the limits $0.5R \leq R \leq 1.5R$, i.e. for R varying within narrow limits.

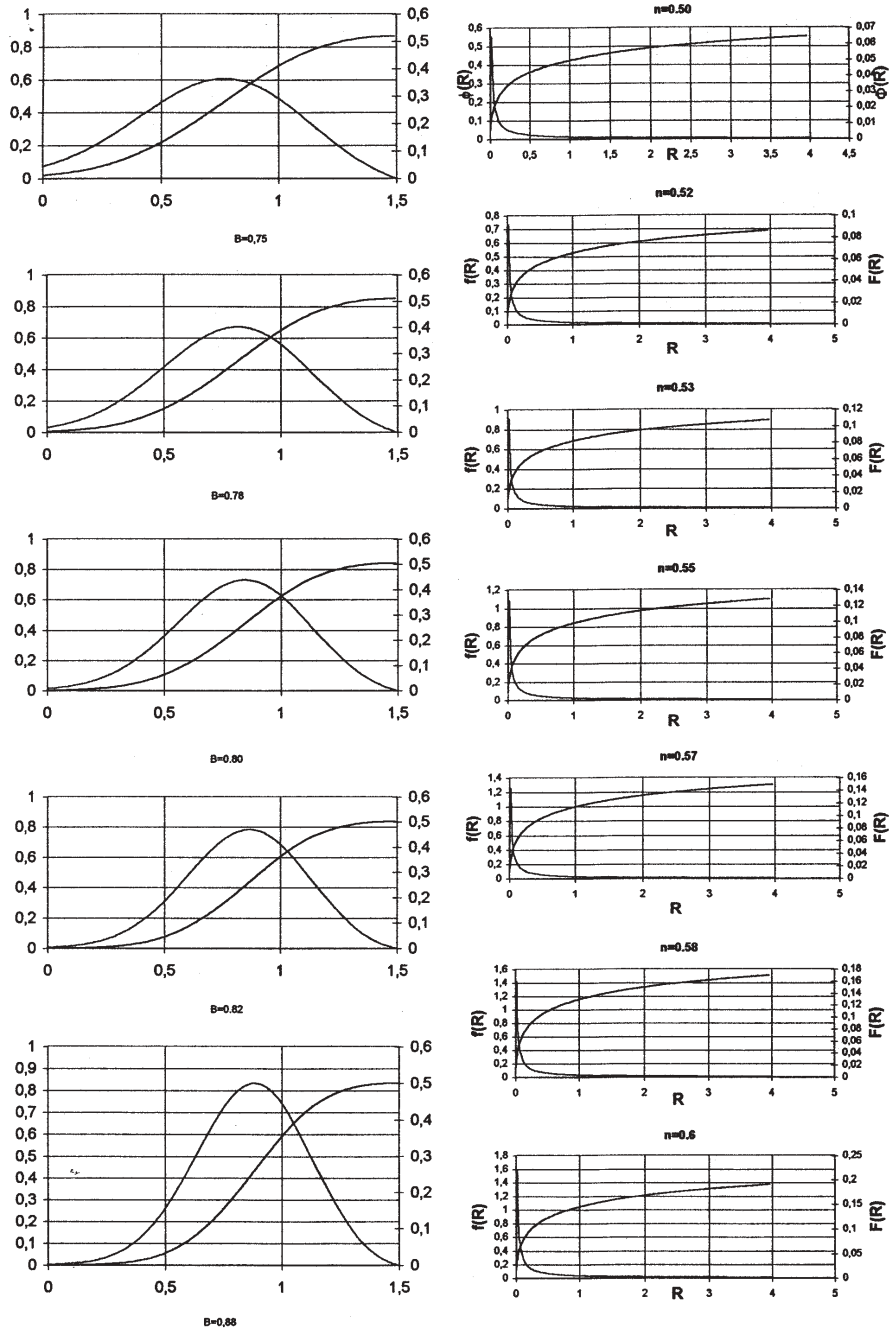


Fig. 7 Density functions and distribution functions: a – for normal distribution, b – for Rosin-Rammler-Sperling distribution in Eq. D1

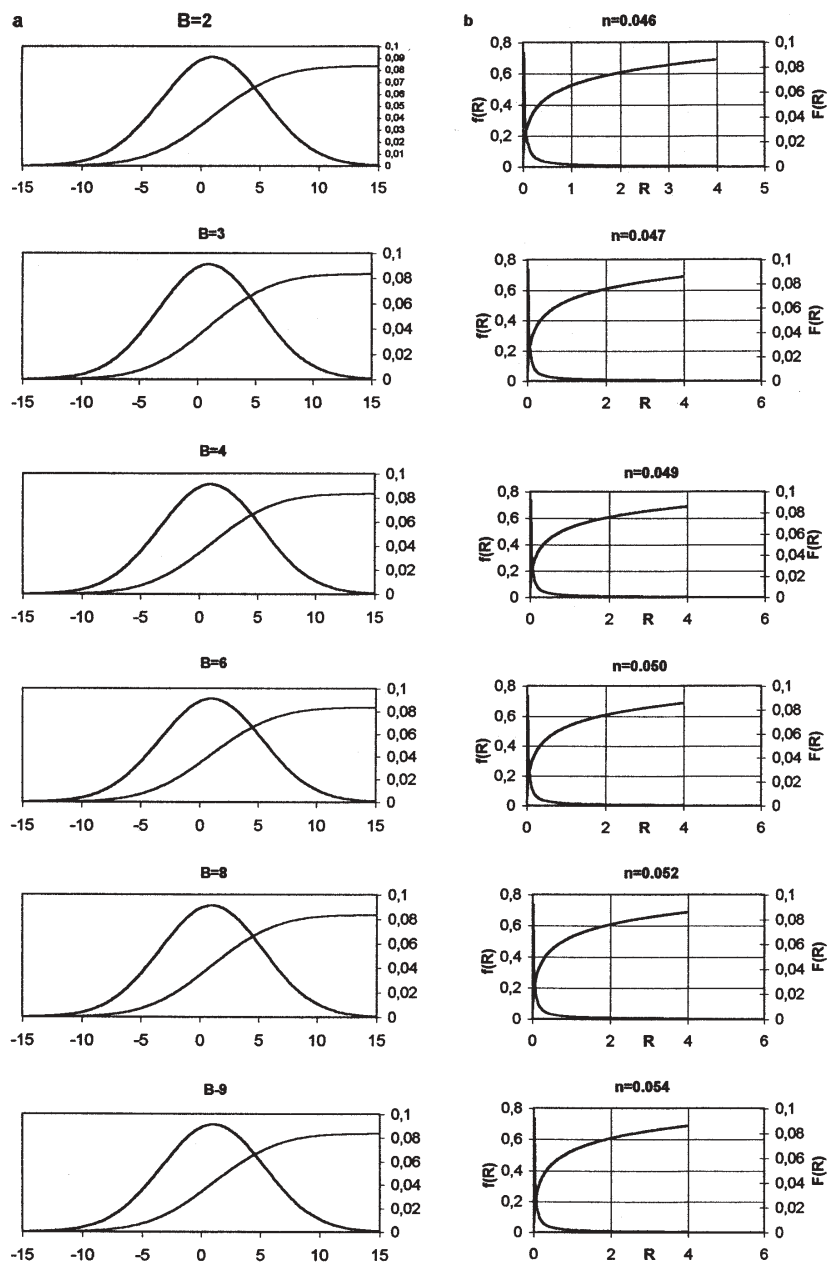


Fig. 8 Density functions and distribution functions: a – for normal distribution, b – for Rosin–Rammler–Sperling distribution in Eq. F2

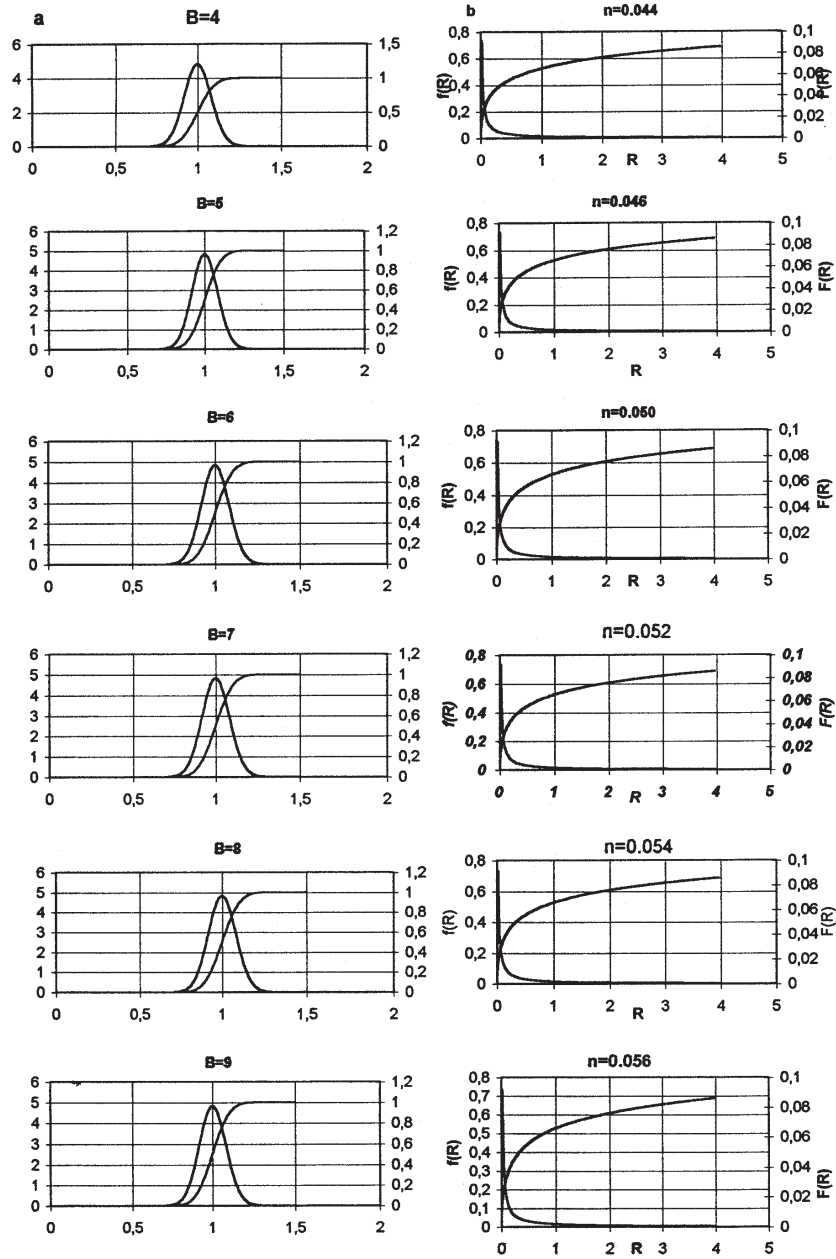


Fig. 9 Density functions and distribution functions: a – for normal distribution, b – for Rosin–Rammler–Sperling distribution in Eq. F3

Table 1a The juxtaposition of obtained kinetic equations describing the mean value of transformation degree $\bar{\alpha}$ for initial Eqs F0, F1, F2, F3 and for normal grain size distribution

Description of equation acc. to [4]	Equation type acc. to [4]	Equations $\alpha=h(t)$ acc. to [4]	Final equations for normal distribution: $\bar{\alpha} =$	Range B	Variation limits of α for B	Reference
F0	α	kt	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} (1-\theta) \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 5; 11 \rangle$	0.013–0.99	[3]
F1	$-\ln(1-\alpha)$	$1 - e^{-kt}$	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} e^{-\theta} \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 3; 7 \rangle$	0.006–0.93	[2]
F2	$[1/(1-\alpha)] - 1$	$1 - [1/kt + 1]$	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} \left(\frac{1}{\theta+1} \right) \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 7; 10 \rangle$	0.0013–0.73	at this paper
F3	$[1/(1-\alpha)^2] - 1$	$1 - (kt+1)^{-1/2}$	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} \left(\frac{1}{\sqrt{\theta+1}} \right) \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 8; 15 \rangle$	0.0013–0.85	at this paper

Table 1b The juxtaposition of obtained kinetic equations describing the mean value of transformation degree $\bar{\alpha}$ for initial Eqs D1, R2, R3 and for normal grain size distribution

Description of equation acc. to [4]	Eq. type acc. to [4]	Eqs $\alpha=h(t)$ acc. to [4]	Final equations for normal distribution: $\bar{\alpha} =$	Range B	Variation limits of α for B	Ref.
D1	α^2	\sqrt{kt}	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} (1-\sqrt{\theta}) \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 0.78; 0.85 \rangle$	0.039–0.47	at this paper
R2	$1 - (1-\alpha)^1$	$1 - (1-kt)^2$	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} (1-\theta)^2 \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 4; 10 \rangle$	0.014–0.882	[3]
R3	$1 - (1-\alpha)^{1/3}$	$1 - (1-kt)^3$	$1 - \left\{ \sqrt{\frac{B}{\pi}} \int_{\theta_1}^{\theta} (1-\theta)^3 \exp[-B(\theta-1)^2] d\theta \right\}$	$B \in \langle 4; 10 \rangle$	0.3–0.9	[1]

Table 2a The juxtaposition of obtained kinetic equations describing the mean value of transformation degree $\bar{\alpha}$ for initial Eqs F0, F1, F2, F3 and for Rosin–Rammler–Sperling’s grain size distribution

Description of equation acc. to [4]	Eq. type acc. to [4]	Eqs $\alpha=h(t)$ acc. to [4]	Final equations for Rosin–Rammler–Sperling’s distribution:	Range n	Variation limits of α for n	Ref.
F0	α	kt	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} (1-\theta_1)\theta^{n-1}\exp[-\theta^n]d\theta\right\}$	0.040–0.05	0.67–0.99	[3]
F1	$-\ln(1-\alpha)$	$1-e^{-kt}$	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} e^{-\theta} \theta^{n-1}\exp[-\theta^n]d\theta\right\}$	0.030–0.09	0.006–0.930	[2]
F2	$[1/(1-\alpha)]-1$	$1-[1/kt+1]$	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} \left(\frac{1}{\theta+1}\right)\theta^{n-1}\exp[-\theta^n]d\theta\right\}$	not used	0.013–0.85	at this paper
F3	$[1/(1-\alpha)]-1$	$1-(kt+1)^{-1/2}$	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} \left(\frac{1}{\sqrt{\theta+1}}\right)\theta^{n-1}\exp[-\theta^n]d\theta\right\}$	not used	0.50–0.235	at this paper

Table 2b The juxtaposition of obtained kinetic equations describing the mean value of transformation degree $\bar{\alpha}$ for initial Eqs D1, R2, R3 and for Rosin–Rammler–Sperling’s grain size distribution

Description of equation acc. to [4]	Eq. type acc. to [4]	Eqs $\alpha=h(t)$ acc. to [4]	Final equations for Rosin–Rammler–Sperling’s distribution:	Range n	Variation limits of α for n	Ref.
D1	α^2	\sqrt{kt}	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} (1-\sqrt{\theta_1})\theta^{n-1}\exp[-\theta^n]d\theta\right\}$	0.50–0.55	0.003–0.92	at this paper
R2	$1-(1-\alpha)^{1/2}$	$1-(1-kt)^2$	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} (1-\theta_1)^2 \theta^{n-1}\exp[-\theta^n]d\theta\right\}$	0.041–0.050	0.045–0.884	[3]
R3	$1-(1-\alpha)^{1/3}$	$1-(1-kt)^3$	$\bar{\alpha}=1-\left\{n\int_{\theta_1}^{\theta} (1-\theta_1)^3 \theta^{n-1}\exp[-\theta^n]d\theta\right\}$	1.0–3.0	0.3–1.0	[1]

In the case of polydisperse material with Rosin–Rammler–Sperling grain size distribution the nature of the distribution depended on the value of parameter n , but the distribution functions and the density functions assumed different forms for various n values (Figs 7–9).

Conclusions

Equation (2) describes the process of thermal dissociation of polydisperse materials with normal grain size distribution for B values ≥ 0.78 . For polydisperse materials with Rosin–Rammler–Sperling grain size distribution the description of the process in terms of that equation is highly effective for $n \geq 0.5$ and large variability ranges of α . Equations F2 and F3 provide a good description of the process of thermal dissociation of solids in the case of normal distribution: Eq. F2 for $B \geq 7$, and Eq. F3 for $B \geq 8$; in the case of Rosin–Rammler–Sperling distributions the Eqs F2 and F3 do not describe the process even for small ranges of variability of α .

A summary of hitherto considerations has been presented in Tables 1a, 1b, 2a and 2b, in which kinetic equations have been given for both types of grain size distribution and variability ranges are given for the limits, in which the initial equations provide a good description of the obtained curves or at least of some fragments of these curves. One may assume, therefore, that thermal dissociation of polydisperse solid materials can not be properly described in terms of kinetic equations in a general case, unless the grain size distribution has been taken into account.

An experimental verification of the results obtained will be presented in the final part of this work.

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