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Analysis of relative rate of reaction/process

Andrzej Mianowski · Tomasz Siudyga

Bretsznajder Special Chapter

Abstract Kinetic or rather thermokinetic analysis of thermal decomposition with releasing gaseous products is a current subject of discussion in many works and still devotes much attention to the property and meaningfulness of the single kinetics triplet determination. Analysis of thermogravimetric data by the relative rate of reaction/process were used to examine the frequently studied process of thermal dissociation of calcium carbonate as a model compound and comparing with published data for chemically defined compounds (azo-peroxyesters) and complex polyolefins–liquid paraffin mixtures. Two methods of correlation between parameters of the model were observed: thermodynamic and analytical expression. It was shown that these relations depend on course of the process. For analyzed model substance, enthalpy of reaction can be deduced on the basis of relation between coefficients in three-parameter equation. For large values of coefficients it is not possible, but other type of correlation was proved. Also, the relative rate of CO_2 gasification (Boudouard reaction) of brown and bituminous coals was analyzed and compared to that of its pyrolysis.

Keywords Relative rate of reaction/process · Thermal decomposition · Kinetics · Enthalpy of reaction · Boudouard reaction

List of symbols

A	Pre-exponential constant in Arrhenius equation, s^{-1}
a	Equilibrium conversion degree of CO_2, $0 \leq a \leq 1$
a_0, a_1, a_2	Coefficients of three-parameter equation (15)
α	Conversion degree, $0 \leq \alpha \leq 1$
E	Activation energy, J mol^{-1}
$f(\alpha)$, $F(\alpha)$	Function of α depending on the reaction mechanism
ΔH	Enthalpy of reaction, J mol^{-1} or J g^{-1}
φ	Multiplex of stoichiometric coefficients
K	Thermodynamic equilibrium constant
m	Mass, mg
N	Number of measurements
v	Stoichiometric coefficient
p	Pressure, Pa
q	Heating rate, K min^{-1}, K s^{-1}
$R = 8.314$ J mol^{-1} K^{-1}	Universal gas constant
R	Relative rate of reaction, K
r versus T	Shortcut of relation (16)
r^2	Determination coefficient
t	Temperature, °C
T	Temperature, K
TG, DTG	Values registered during thermogravimetric measurement, in mg and mg K^{-1} respectively
τ	Time, s

Subscripts

i	Initial state or natural number
eq	Equilibrium
g	Gaseous

A. Mianowski · T. Siudyga (✉)
Department of Chemistry, Inorganic Technology and Fuels,
Silesian University of Technology, B. Krzywoustego 6,
44-100 Gliwice, Poland
e-mail: tomasz.siudyga@polsl.pl

m	Maximal
r	Experimentally determined point of intersection of linear relations (33)
s	Solid
□	Standard
*	Equilibrium

Introduction

In the most common cases of the reactions associated with typical chemical analysis, mass is reduced [1]:

$$\nu_A A_{(s)} \rightarrow \nu_B B_{(s)} + \nu_C C_{(g)} \qquad (1)$$

$$(\text{simple example: } CaCO_3 \leftrightarrow CaO + CO_2\uparrow, \nu = 1) \qquad (1a)$$

$$\nu_A A_{(s)} \rightarrow \sum \nu_C C_{(g)} \qquad (2)$$

$$\big(\text{complicated example: } 4NH_4ClO_4 \rightarrow 4HCl\uparrow + 2N_2\uparrow + 5O_2\uparrow + 6H_2O\uparrow,\ \Sigma\nu_i = 17/4\big) \qquad (2a)$$

For reactions (1) and (2), thermodynamic equilibrium constant can be described:

$$K \equiv \prod \left(\frac{p_i^*}{p^\theta}\right)^{\nu_i} \qquad (3)$$

If we assume that the partial pressure of particular gaseous product is the result of stoichiometry of reaction then for every particular gaseous product released in the reaction, the following dependence can be expressed as:

$$\frac{p_i^*}{p^\theta} = \frac{\nu_i}{\sum \nu_i}\alpha_{eq} \qquad (4)$$

After considering Eq. (4), Eq. (3) takes a form:

$$K = \alpha_{eq}^{\sum \nu_i}\varphi, \quad \text{where } 0 \le \alpha_{eq} \le 1 \text{ and } \varphi = \prod \left(\frac{\nu_i}{\sum \nu_i}\right)^{\nu_i}. \qquad (5)$$

When $\nu = \nu_i$ and $\Sigma\nu_i = \nu_i$ and in consequence $\varphi = 1$, relation (5) has a very simple form [2]:

$$K = \alpha_{eq}^{\nu} \qquad (6)$$

For reactions in which more than one gaseous product is released ratio of stoichiometric coefficients φ has to be considered. The value of φ tends to be zero with increasing multiplicity of gaseous products.

For relation (3), it is necessary to point out the other limitation, which is also clearly observed in logarithmic form—assuming limitation ($0 \le \alpha_{eq} \le 1$) one can obtain value of K for $\alpha_{eq} = 1$

$$K_{\alpha_{eq}=1} = \varphi. \qquad (7)$$

When many gaseous products are released in thermal decomposition of solid ($i > 1$), one can conclude that thermodynamic equilibrium constant is very small, close to zero. In the case of reaction (2a), limitation $0 \le \alpha_{eq} \le 1$ is fulfilled for $0 \le K \le 36.65 \times 10^{-4}$. It should be noted that Eq. (2a) is only a summary recording of the process, which consists of elementary reactions, each one is described by individual value of the constant K [3–6]. Hence the determination of K value calculated according to (6) for the stoichiometry (2a) has to be incorrect. However, thermal analysis in many cases allows for separation of individual elementary reactions, so that ratio in Eq. (4) $\varphi = \prod (\nu_i/\sum \nu_i)^{\nu_i} \rightarrow 1$. TGA studies indicate the possibility of isolating at least two stages of decomposition NH_4ClO_4, each one has to be considered separately [4]. However, other analytical methods of product identifying are often required for detailed analysis of the stoichiometry of the individual steps.

By substituting Eq. (5) after applying logarithms:

$$\ln K = \Sigma\nu_i \ln\alpha_{eq} + \ln\varphi, \qquad (8)$$

and differentiating in terms of temperature T one can finally obtain:

$$d\ln K/dT = \Sigma\nu_i\big(d\ln\alpha_{eq}/dT\big). \qquad (9)$$

The van't Hoff's equation was originally formulated for concentrations and is now used for activities. Hence, it has to be taken into account. Therefore, the basis for further considerations is the expression (10), whereas the stoichiometric coefficient ν is represented by a single gaseous substance, which for complex pyrolysis processes (or even complex chemical compounds such as [7]) is a simplification and it is difficult to assume the existence of equilibrium in thermodynamic sense as reference to the constant K. After differentiation (9), multiplex of stoichiometry coefficients φ loses its importance. It is valid when we wanted to calculate constant K according to formula (5) from known α_{eq}.

Using van't Hoff's isobar for reactions (1) and (2) [7–9]:

$$\left(\frac{\partial \ln K}{\partial T}\right)_p = \frac{\Delta H}{RT^2} \qquad (10)$$

and assuming for both types of reactions (1) and (2) that $\Sigma\nu_i = \nu$ as a stoichiometric coefficients for gaseous products, Eq. (10) is valid in form (when $P = P^\theta$):

$$\frac{d\alpha_{eq}}{dT} = \alpha_{eq}\left(\frac{\Delta H}{\nu RT^2}\right), \qquad (11)$$

and according to Błażejowski considerations [10, 11]:

$$\ln\alpha_{eq} = \frac{\Delta H}{\nu R}\left(\frac{1}{T_{eq}} - \frac{1}{T}\right). \qquad (12)$$

It means in accordance with $0 \le \alpha_{eq} \le 1$, the left side of (11) takes values:

$$0 \leq \frac{\mathrm{d}\alpha_{\mathrm{eq}}}{\mathrm{d}T} \leq \frac{\Delta H}{\nu R T_{\mathrm{eq}}^2}, \tag{13}$$

and the maximum of the function is outside the investigated range, i.e., for $T \ggg T_{\mathrm{eq}}$ ($T_{\mathrm{m}} = \Delta H/2\nu R$) [12].

Remarks on the relative rate of reaction/process

After transformations, the modified van't Hoff's equation (12) may be symbolically presented as:

$$\ln \alpha_{\mathrm{eq}} = a_0 - \frac{a_1}{T}. \tag{14}$$

While the experimentally obtained conversion degree is described by three-parameter equation [13]:

$$\ln \alpha = a_0 - \frac{a_1}{T} - a_2 \ln T \tag{15}$$

which can be reduced to a linear dependence of the relative rate of the reaction/process [14]:

$$r = a_1 - a_2 T, \tag{16}$$

where

$$r = \frac{\mathrm{d}\alpha}{\alpha \mathrm{d}T} T^2. \tag{17}$$

Expression (17) means derivative scaled in terms of temperature and slightly differs from the typical definition of the relative rate [15]. Dependence (17) can be expressed directly from values obtained in thermogravimetric analysis:

$$r = -\frac{\mathrm{DTG}}{m_{\mathrm{i}} - \mathrm{TG}} T^2, \tag{18}$$

where weight m_{i} should be replaced by new value for successive maximum temperature initiating further steps. Relation (18) is a direct method of description of reaction and also complicated process in terms r versus T.

Equation (11) can be expressed identically to formulae (16) and (17) for $a_2 = 0$:

$$r_{\mathrm{eq}} = \Delta H/\nu R = a_1 = \mathrm{const} \tag{19}$$

so it is a linear relation parallel to the axis of T and means the equilibrium state in the sense of Eq. (12).

Further analysis of Eqs. (16–18) leads to simplified temperature relation (20) determined for linear mass loss versus temperature:

$$r = \frac{T^2}{T - T_i} \tag{20}$$

and is called as activationless temperature profile of zeroth-order. Our experience indicates that the curve (20) is a restriction and corresponds to the minimum values of the r.

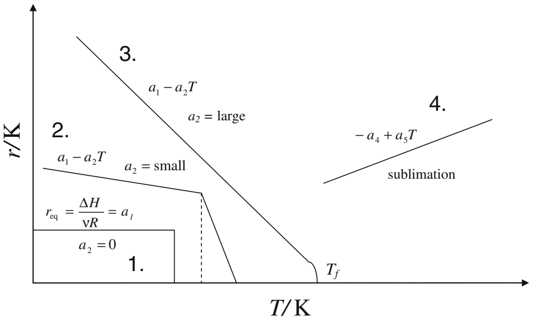


Fig. 1 Typical dependences of relative reaction rate versus temperature: (*1*) equilibrium process according to (19), (*2*) near-equilibrium process [28], (*3*) linear relation (16), (*4*) linear relation with reversed signs in comparison with (16)—physical process (sublimation—according to [29])

Aim of the work—relative rate of reaction/process

Typical dependences for chemical reactions according to (16) and (19) are shown in Fig. 1.

In accordance of phenomenological approach, in this work for the equilibrium state, *ex definitione*, we assume $a_2 = 0$ in Eq. (16) which implies Eq. (19) and $\varphi = 1$ without considering all the elements specifying this state (e.g., heat and mass flows). This assumption relates to the chemically defined compounds. Continuing near–equilibrium state can be determined when a_2 is small ($a_2 < 200$). It should be noted that even if $a_2 = 0$, we are not able to distinguish the origin of this equation: van't Hoff's isobar (14) or Szarawara's temperature criterion [13, 27, 31].

For complex reactions (pyrolysis of polyolefins or coals), stoichiometry is unknown and relationship (12) is applicable only for selected elementary reactions, such as releasing of H_2O, CO_2, CH_4, H_2, and N_2. Equation (15) has an empirical character, but coefficient a_2 fulfills the criteria of kinetic measure. In the case of CO_2 gasification of coals, reactions (1) or (2) are not maintained and chemical equilibrium constant (3) is determined with disregarding the solid phase, and it can be expressed by equilibrium conversion degree of CO_2 as $K = 4a^2/(1 - a)^2$, where a is equilibrium conversion degree of CO_2 [25].

Hence the nature of a_2 coefficient is dualistic [8] and other studies are required to more detailed analysis of reaction/process.

The work is intended to synthetic presentation of the results of previous works using our own conception of relative rate of reaction/conversion in form (18) with the additional possibility which gives the restriction (20) where it seems to be sensible.

Results and discussion

Assuming comments resulting from the equation (11), the left side can be written as:

$$\frac{d\alpha_{eq}}{dT}=\frac{d\alpha_{eq}}{d\tau}\frac{d\tau}{dT}=\frac{d\alpha_{eq}}{d\tau}\frac{1}{q}\quad \text{for } q>0. \tag{21}$$

Expression $d\alpha_{eq}/d\tau = 0$ when $q = dT/d\tau = 0$, i.e., for isothermal conditions. In dynamic condition, equation (21) should be interpreted as a form proposed by Holba and Šesták [16]:

$$\frac{d\alpha_{eq}}{d\tau}=\frac{d\alpha_{eq}}{dT}\frac{dT}{d\tau}=\frac{d\alpha_{eq}}{dT}\quad q\neq 0 \tag{22}$$

It is assumed that for equilibrium conversion degree, the expression (21) equals 0 [16, 17], and in such a situation, we have $\alpha_{eq} = 1$. According to Eq. (13) for $T \geq T_{eq}$, reaction above this temperature is irreversible [17]. Because increase in conversion degree ($\alpha \rightarrow \alpha_{eq}$) with temperature enhancing is observed, i.e., $d\alpha/dT > 0$, it is convenient to assume that under dynamic conditions, reaction comes to equilibrium state in the sense of Eq. (5) but it is not achieved, as shown in [18]. This fact was noted much earlier and discussed in publications [2, 10, 11, 19, 20]. Even if in experimental conditions we obtain $\alpha = \alpha_{eq}$ then $d\alpha_{eq}/dT \neq 0$ because Eq. (22) is valid and flow of mass and heat occurs. Therefore, this condition can be considered as stationary, but not equilibrium.

We analyze the kinetics in dynamic conditions ($q > 0$) [10, 11]:

$$\frac{d\alpha}{dT}=\frac{k}{q}f(\alpha)\left[1-\frac{K_{\alpha}}{K}\right], \tag{23}$$

where K_{α} is the analog of product of the instantaneous activities, and K is the thermodynamic equilibrium constant. If $K_{\alpha}/K = 1$ then $\alpha = \alpha_{eq}$, and the reaction rate reaches value of 0, and for the $K_{\alpha}/K \rightarrow 0$ one can obtain the typical kinetic or thermokinetic equation.

In the simplest case, when equilibrium constant is described by Eq. (5), Eq. (23) can be written as [12, 17]:

$$\frac{d\alpha}{dT}=\frac{k}{q}f(\alpha)\left[1-\left(\frac{\alpha}{\alpha_{eq}}\right)^{v}\right]. \tag{24}$$

Possible interpretation indicates that coefficient v modifies the part of the equation related to α/α_{eq}, and it may be the source of kinetic compensation effect (KCE, expression $f(\alpha)\left[1-\left(\alpha/\alpha_{eq}\right)^{v}\right] = F(\alpha)$ became a new form of function f(α)).

For each system, there is a range of temperatures where substrates and products are in equilibrium. Below this range the substrates are more stable, while above the range the products are stable. Choosing interval, temperature of isothermal kinetics can be studied. For non-isothermal conditions, Gibbs free energy is always negative enough to be able to accept that value of the thermodynamic stimulus equals 1. This is an important advantage for the conduct of the kinetic analysis of non-isothermal conditions [21].

Starting from the Holba–Šesták equation [16] for dynamic if we assume that the rate of reaction is higher than zero, the following condition has to be fulfilled [17]:

$$d\alpha/d\tau - \alpha q\left(d\ln \alpha_{eq}/dT\right) \geq 0 \quad q>0, \tag{25}$$

after transformations leads to inequality:

$$d\alpha/d\tau \geq \alpha q\left(d\ln \alpha_{eq}/dT\right). \tag{26}$$

As a consequence, one can obtain:

$$d\ln \alpha/dT \geq d\ln \alpha_{eq}/dT. \tag{27}$$

If we multiply the both sides of inequality (27) by T^2, we obtain relation $r \geq r_{eq}$. Starting from Eq. (27) and for equal differentials dT (Fig. 2), we come to relation:

$$\frac{d\alpha}{d\alpha_{eq}} \geq \frac{\alpha}{\alpha_{eq}} \tag{28}$$

which implies two possibilities:

1. When $d\alpha = d\alpha_{eq} = \Delta\alpha$, we can obtain:

$$1 \geq \frac{\alpha}{\alpha_{eq}}, \tag{29}$$

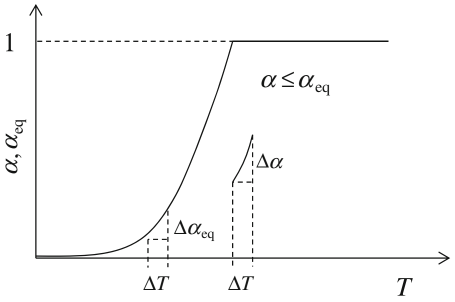


Fig. 2 Relations between α and α_{eq} observed in dynamic conditions

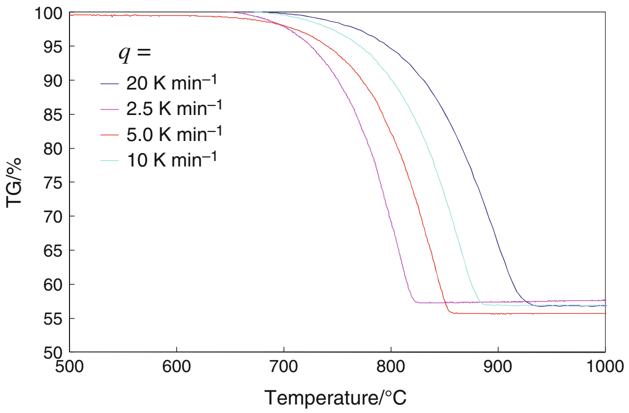


Fig. 3 Comparison of TG curves for different heating rates ($CaCO_3$)

Fig. 4 Relations *r* versus *T* for $CaCO_3$ decomposition

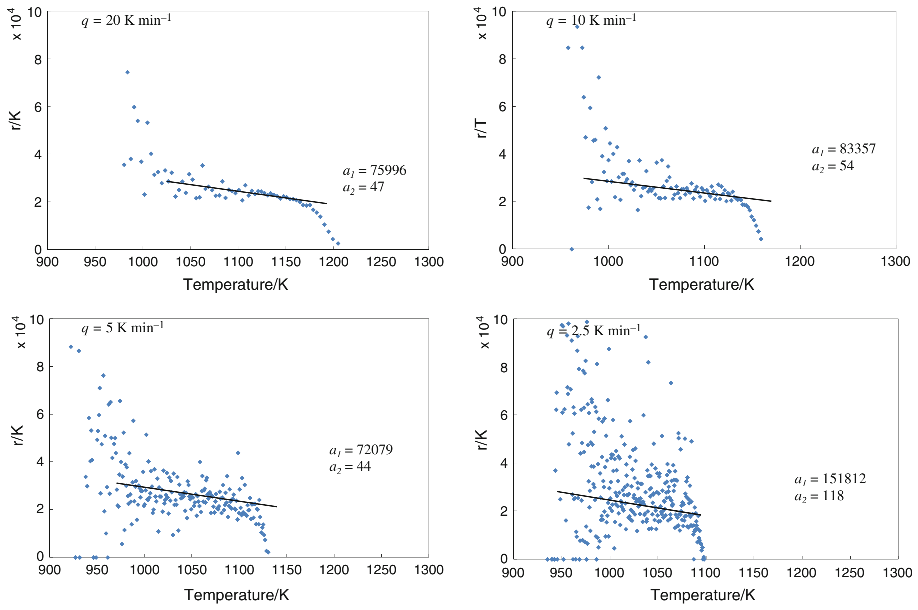


Table 1 Coefficients obtained from the fitting of thermogravimetric data with the three-parameter equation

q/K min^{-1}	a_1/K	a_2	r^2	T_m/K
2.5	1,51,812	118	0.1615	1,082
5	72,079	44	0.2851	1,114
10	83,357	54	0.5341	1,142
20	75,996	47	0.8345	1,172

and in consequence

$$\alpha \leq \alpha_{eq} \tag{30}$$

because relation α versus T is shifted toward higher temperatures in comparison with equilibrium and result of thermodynamic efficiency $\eta \leq \alpha/\alpha_{eq}$.

2. Starting from Eq. 27, the following inequality can be also derived:

$$d\ln\frac{\alpha}{\alpha_{eq}} \geq 0 \tag{31}$$

which means a tendency to approach α to α_{eq} with increasing temperature *T* (steepness, not marked on Fig. 2)

Starting from Eq. (31), one can obtain relation (27) and conclude that:

$\mathrm{d}\ln\alpha/\mathrm{d}T \geq \Delta H/vRT^2$ and after integration

$$\ln\alpha \geq \frac{\Delta H}{vR}\int\frac{\mathrm{d}T}{T^2} + \mathrm{const} \tag{32}$$

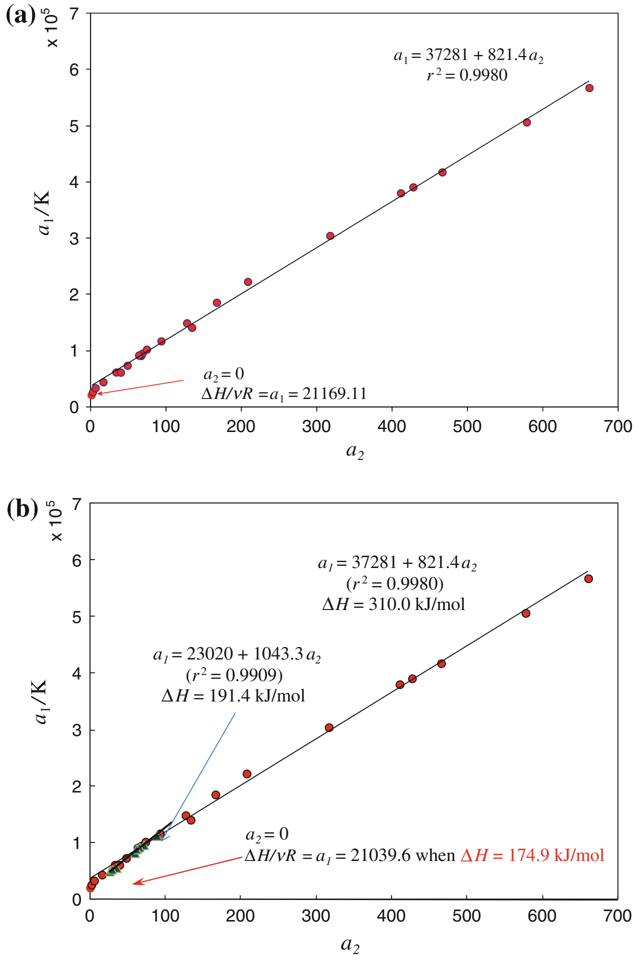


Fig. 5 Dependence between coefficients in three-parameter equation for $CaCO_3$: **a** data obtained in this work, **b** literature results [8, 30]

what corresponds with Błażejowski considerations [10, 11, 19].

When it is equality, this relation can be symbolically given as Eq. (14) but in order to describe experimentally obtained conversion degree, the element ($-a_2 \ln T$) was introduced—Eq. (15).

Thermal dissociation of $CaCO_3$

Studies on the thermal dissociation of $CaCO_3$ (calcite) presented in [8] were repeated, in order to decide which of the Eqs. (33) and (34) is more appropriate to describe the experimental data:

Relations between parameters in Eq. (16) can be described by two expressions:

1. Thermodynamic correlation [8]:

$$a_1 = \frac{\Delta H}{vR} + a_2 T_r \tag{33}$$

2. Analytical [7]:

$$a_1 = T_m\left(1 + a_2 + \sqrt{1 + a_2}\right), \quad a_2 \ggg 0. \tag{34}$$

TG curves for $CaCO_3$ for different heating rates are presented on Fig. 3.

On the basis of Eq. (18), relative rates of reaction were calculated and relations r versus T were obtained—Fig. 4. Values of parameters from Eq. (16) are presented in Table 1.

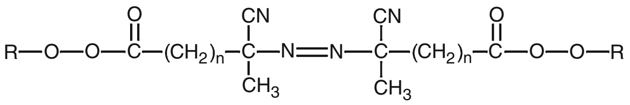
It was found that determination coefficient (r^2) strongly depends on heating rate for $CaCO_3$ thermal decomposition. But it has to be pointed out that for every case relation r versus T is generally the same type—relation 2 on Fig. 1.

Both dependences (33) and (34) are evidence of considerable importance the a_2 coefficient and the existence of the effect of close to isokinetic nature.

It was shown that for low values of a_2, process occurs under conditions close to equilibrium. In this case, enthalpy of reaction can be deduced on the basis of relation a_1 versus a_2—Fig. 5. For large values of a_2, it is not possible, but the values of $T_{m(calc)}$ are close to the T_m.

Thermal decomposition of azo-peroxyesters

Analysis of relative rate of reaction was also performed for thermal decomposition of chemically defined compounds: azo-peroxyesters—Scheme 1.



$$R{-}O{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_n{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CN}{|}}{C}}{-}N{=}N{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CN}{|}}{C}}{-}(CH_2)_n{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}O{-}R$$

Scheme 1 The compounds investigated: **1** ($n = 2$, R = *t*-Bu), **2** ($n = 3$, R = *t*-Bu), **3** ($n = 4$, R = *t*-Bu), **4** ($n = 2$, R = *t*-Am), **5** ($n = 3$, R = *t*-Am), **6** ($n = 4$, R = *t*-Am)

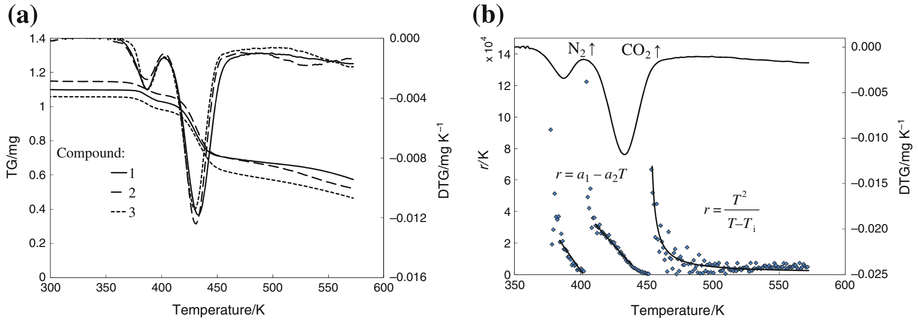


Fig. 6 Thermal decomposition of azo-peroxyesters [7]: **a** TG/DTG curves, **b** relation r versus T (*numbers* indicate the compounds investigated—for details see Scheme 1)

Table 2 Coefficients obtained from the fitting of thermogravimetric data with the three-parameter equation

No.	First stage					Second stage				
	a_1/K	a_2	r^2	T_m/K	ΔT_m/K	a_1/K	a_2	r^2	T_m/K	ΔT_m/K
1	4,61,783	1,155	0.940	387	−0.5	3,32,953	739	0.982	432	−2.3
2	3,61,261	904	0.916	386	−0.4	4,48,739	1010	0.971	429	−2.2
3	4,87,854	1,215	0.929	384	−6.0	4,17,934	939	0.969	428	−2.5
4	3,29,361	822	0.907	383	−3.5	5,02,316	1140	0.991	426	−0.8
5	3,34,129	833	0.915	386	−1.1	4,84,354	1100	0.985	424	−2.9
6	3,23,292	804	0.901	387	−0.8	4,48,781	1020	0.985	425	−1.8

Values of T_m(calculated) were derived by using Eq. (34); $\Delta T_m = T_m(\text{calculated}) - T_m(\text{measured})$

It was proved that this process proceeds in two stages—N_2 is released in the first and CO_2 in the second. The mass loss seen on the TG curves indicates that after the second stage other volatile products are evolved.

Plots of r versus T are presented in Fig. 6. Their linear sections correspond to quite a wide range of α values—from 0.2 to 0.9 for the first stage and from 0.05 to 0.9 for the second one. This follows findings, which show that it is very convenient to apply the relative rate of thermal decomposition for this type of chemical compounds.

Values of a_1, a_2, and ΔT_m for both decomposition stages are presented in Table 2. Calculated values of T_m are generally lower than its measured values, although both sets of values correspond quite well to each other. This implies that our approach is reliable.

Values of a_2 are relatively high: 804–1,215 for the first stage of thermal decomposition and 739–1,140 for the second. They are typical of chemical processes rather than physical ones. The rate of mass loss after these two stages can be obtained from relationship (20), which appears to be formally a zeroth-order activationless process.

Relations between a_2 and E can be grouped on the basis of differences in the structures of the compounds (**1–3** and **4–6**) and the stages of decomposition (Fig. 7). Linear trends are observed for a given group of compounds and stage of the process. This may indicate that chemical structure is the main factor affecting the kinetic characteristics of thermal decomposition.

Thermal decomposition of polyolefins

Analysis of thermogravimetric files using the relative rate of the process were also used to examine the pyrolysis process of complex mixtures, such as for the thermal and thermo-catalytic decomposition of polyolefins [9, 22]. Exemplary relations for polyolefins–liquid paraffin mixtures are presented on Fig. 8.

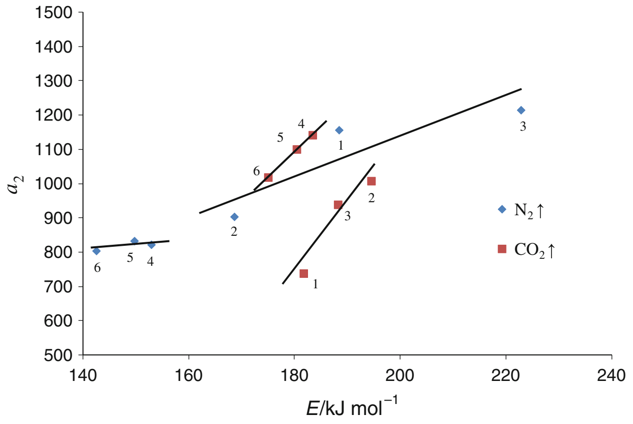


Fig. 7 Dependence of a_2 coefficient versus activation energy (E) for azo-peroxyesters (*numbers* indicate the compounds investigated—for details see Scheme 1)

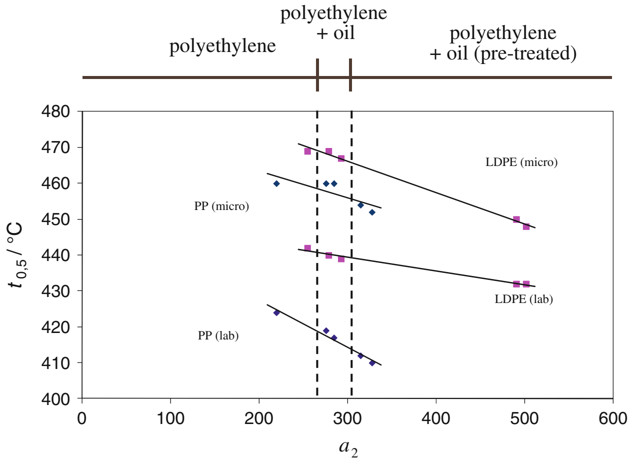


Fig. 9 Relationship between coefficient a_2 (microscale) and characteristic temperature of the process (corresponding to 50 % conversion, $t_{0.5}$—both micro- and laboratory scale)

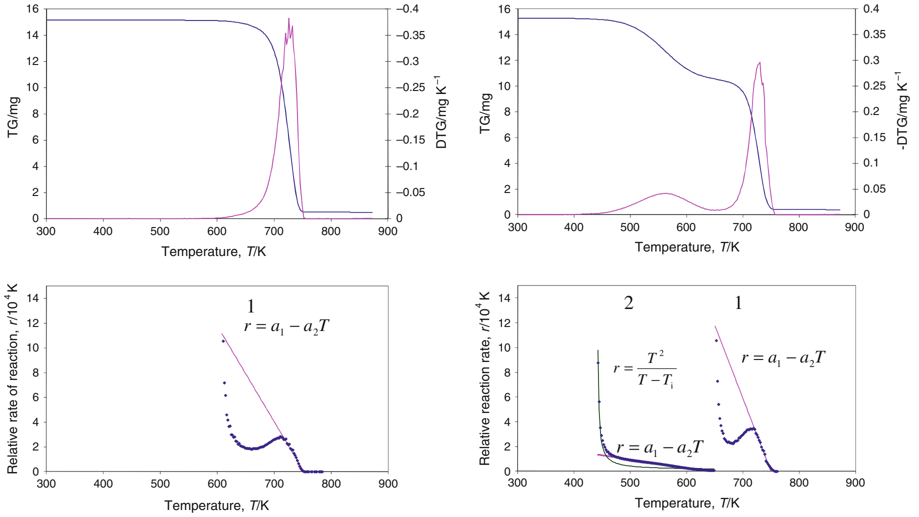


Fig. 8 Relative rate of thermal decomposition of polyethylene LDPE with paraffin oil (*1* decomposition of polyethylene, 2 decomposition of paraffin oil)

Table 3 Raw materials for studies (by-products)

No.	Sample	Form	Molecular mass/g mol^{-1}
1	HDPE (Polimeri Europa)	Powder	0.8×10^6
2	**LDPE (Braskem Utec)**	Powder	1.2×10^6
3	**HDPE (Arcoplast)**	Powder	1.5×10^6
4	LLDPE (Polimeri Europa)	Powder	1.3×10^6
5	HDPE (Slovnaft Petrochemicals)	Powder	1.0×10^6
6	HDPE (Ticona LLC)	Granules	1.5×10^6
7	HDPE (Ticona LLC)	Granules	1.0×10^6
8	LDPE (Slovnaft Petrochemicals)	Granules	0.8×10^6

Samples in bold were selected for further detailed studies

Table 4 Coefficients obtained from the fitting of thermogravimetric data with the three-parameter equation

No.	a_1/K	a_2	r^2	$\frac{a_1 - a_{1(\mathrm{calc})}}{a_1} \times 100\,\%$	$\Delta T_\mathrm{m}/K$
1	2,751,359	3,561	0.9891	1.8	13.5
2	2,350,379	3,062	0.9845	1.3	9.6
3	2,780,508	3,594	0.9955	1.5	11.6
4	2,423,649	3,153	0.9896	2.0	14.8
5	3,058,729	3,962	0.994	1.4	10.6
6	1,875,021	2,424	0.9891	2.6	19.7
7	3,235,678	4,195	0.9916	1.6	12.3
8	2,459,059	3,185	0.9856	1.6	12.2

Values of T_m(calculated) were derived by using Eq. (34); $\Delta T_\mathrm{m} = T_\mathrm{m}$(calculated) $-$ T_m(measured)

Table 5 Coefficients obtained from the fitting of thermogravimetric data with the three-parameter equation (L, LDPE series; H, HDPE series)

Sample	Conditions: T_f; time in T_f; q	a_1/K	a_2	r^2	$\frac{a_1 - a_{1(\mathrm{calc})}}{a_1} \times 100\,\%$	ΔT_m/K
1H	420 °C; 15 min; 9 K/min	98,444	115	0.9899	2.5	19.4
2H	420 °C; 15 min; 7 K/min	1,24,689	150	0.9553	1.0	7.5
3H	420 °C; 25 min; 7 K/min	84,948	97	0.8882	2.0	43.1
4H	420 °C; 30 min; 8 K/min	45,207	44	0.9622	0.8	122.1
5H	410 °C; 15 min; 7 K/min	1,44,184	176	0.9592	0.3	2.5
6H	410 °C; 30 min; 6 K/min	1,08,942	129	0.9543	1.7	13.3
7H	380 °C; 15 min; 8 K/min	1,92,923	241	0.8781	-0.8	-2.1
8H	380 °C; 30 min; 8 K/min	1,43,434	175	0.9388	1.0	7.7
1L	420 °C; 15 min; 9 K/min	71,451	79	0.9474	0.8	62.2
2L	420 °C; 15 min; 7 K/min	1,37,436	167	0.9787	1.4	10.3
3L	420 °C; 25 min; 7 K/min	73,700	82	0.9824	2.2	60.0
4L	420 °C; 30 min; 8 K/min	28,710	22	0.9611	1.4	297.7
5L	410 °C; 15 min; 7 K/min	1,54,682	190	0.9819	1.4	10.1
6L	410 °C; 30 min; 6 K/min	1,15,691	138	0.9457	2.4	18.1
7L	380 °C; 15 min; 8 K/min	1,71,178	212	0.9220	0.8	6.0
8L	380 °C; 30 min; 8 K/min	60,953	65	0.9627	2.5	74.2

Values of T_m(calculated) were derived by using Eq. (34); $\Delta T_\mathrm{m} = T_\mathrm{m}$(calculated) $-$ T_m(measured)

Determined values of a_2 coefficient are relatively small for the first stage of thermal decomposition, where physical processes dominate (distillation and, to a less extent, paraffin oil thermal decomposition). In case of the second stage connected with polymer decomposition coefficient, a_2 takes on significantly higher values.

Relations between composition and preparation of samples was also found—Fig. 9 [22].

Thermal decomposition of waste products from polyolefins production (LDPE and HDPE) and polyolefin waxes was also studied by relative rate of reaction/process. Samples obtained in different temperatures and for different time of reaction were studied in TGA measurements. Different polyethylenes were used as raw materials—Table 3. Results for particular polymers used in studies are presented in Table 4.

Determined values of a_2 for waxes are large in comparison with obtained waxes (Table 5). As was mentioned above in this case, relation (34) gives values of $T_{\mathrm{m(calc)}}$ corresponded to experimental data, and there is no possibility to deduce enthalpy of reaction on the basis of relation a_1 versus a_2.

The same calculation procedure was performed for waxes obtained from selected polyethylenes—according to procedure described in "Experimental". Results are presented in Table 5.

Determined values of a_2 for waxes are relatively small in comparison with original polyethylenes, so one can conclude that physical processes (distillation low molecular fractions and less extent thermal decomposition) dominate—Fig. 10. It was also found that relation (34) gives values of $T_{\mathrm{m(calc)}}$ corresponded to experimental data only for relatively high values of a_2—for original polymers. When these values are small, differences between T_{m} and $T_{\mathrm{m(calc)}}$ are very large. For $a_2 = 22$: ΔT_{m} equals almost 298 K, whereas for $a_2 = 241$, $\Delta T_{\mathrm{m}} = -2.1$ K.

Enthalpy of wax decomposition cannot be obtained directly from intercept in linear relationship $a_1 = 749.8a_2 + 12{,}214$ because stoichiometry in unknown and coefficient ν for gaseous products is difficult to determine. Even if we take into account the values of energetic effects from DSC (495 J/g) [23], the calculated value of ν has to be very small ($\nu \lll 1$) which is in contradiction with the fact that large amount of gaseous products is released in the process. Although equations r versus T [Eqs. (16) and (17) in form (18)] have a very good fit, they are only very useful empirical relationship, but without reference to the ΔH.

The influence of decomposition conditions on a_2 value is observed—Fig. 11. The influence of final temperature and time of the process on the wax properties can be also clearly observed. The a_2 value decreases with increasing temperature and time of the process. It is possible to

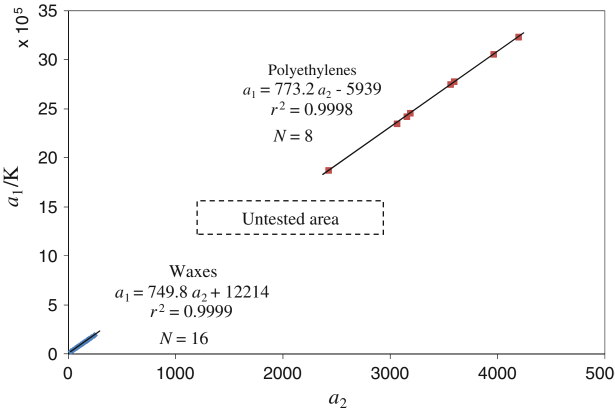


Fig. 10 Dependence between coefficients in three-parameter equation for polyethylenes and waxes

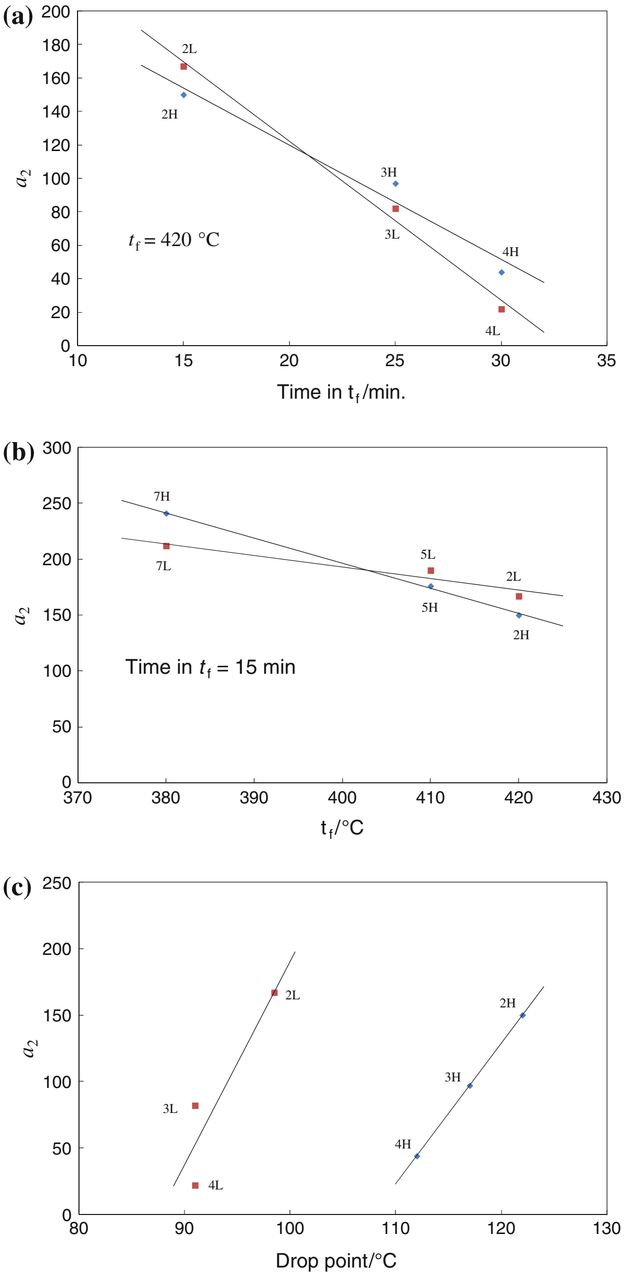


Fig. 11 Empirical dependences of a_2 versus conditions of thermal decomposition process and selected properties of the waxes: **a** a_2 versus time of heating in $t_{\mathrm{f}} = 420$ °C; **b** a_2 versus t_{f} for $\tau = 15$ min; **c** a_2 versus drop point time of heating in $t_{\mathrm{f}} = 420$ °C

Fig. 12 Relative rate of coals decomposition in N_2: **a** brown coal, **b** bituminous coal—drying (*I*); pyrolysis (*II*)

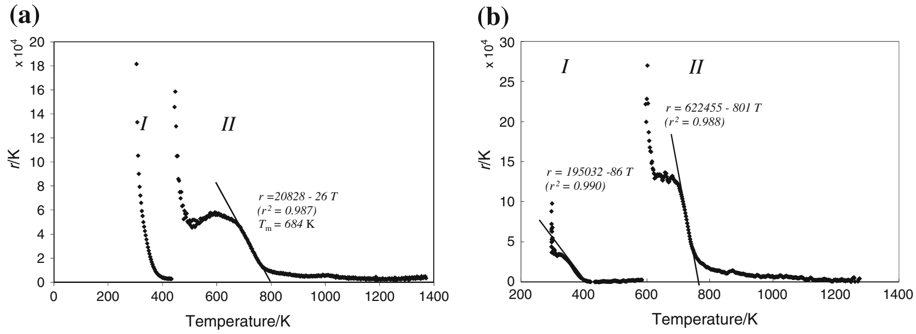
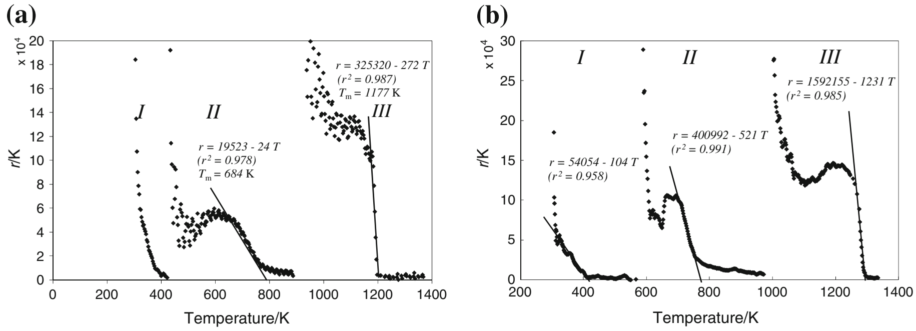


Fig. 13 Relative rate of CO_2 gasification of coals: **a** brown coal, **b** bituminous coal—drying (*I*); pyrolysis (*II*); Boudouard reaction (*III*)



approximate these relations for all analyzed samples (dashed lines in Fig. 1). Relation between a_2 and drop point of the waxes is also observed, but in this case two relations (for LDPE and HDPE series) are separated. The present approach allows to connect the analyses of thermal decomposition in micro- and laboratory scales.

Coals

Gasification of coals is an important direction of research for years [24]. In the atmosphere of CO_2, Boudouard–Bell reaction occurs [25], usually called the Boudouard reaction [24, 26]. The present authors have also conducted similar type of studies previously [27].

In this work, relative rate of the process were used to examine the pyrolysis (N_2 atmosphere) and CO_2 gasification of bituminous and brown coals—Figs. 12 and 13.

On the basis of the course of r versus T one can conclude that in both cases (N_2 and CO_2) the first stage of decomposition refers to drying, whereas the second one concerns with pyrolysis (similar values of parameter a_2 in both cases). Number of studies showed that for the chemically defined compounds, thermal decomposition proceeds according to near-equilibrium curve 2 on Fig. 1—in the sense of Eq. (12). Whereas for complex chemical processes, relation r versus T usually proceeds according to curve 3 on Fig. 1. Nature of a_2 coefficient is dualistic [8] and in this case it has a kinetic character.

In the case of CO_2 gasification, the third stage is also observed. It was observed that values of a_2 are generally higher for CO_2 gasification, and we additionally conclude that pyrolysis process occurs similarly (influence of CO_2 is not observed). It was also proved that in every case of bituminous coals higher values of a_2 are obtained than brown coals. It is the result of differences in their structures and composition, and thus thermal stability and reactivity. These are very interesting issues and will be analyzed in the subsequent works.

It was also found that the method of the relative rate of reaction/process suited much better to analyze complex processes of decomposition of various chemical substances and their mixtures.

Experimental

The use of relative rate for describing thermal decomposition of materials was considered in these studies. Therefore, TGA analysis model substances ($CaCO_3$) as well as complex substances such as polyolefins and coals were performed. CO_2 gasification process was also considered for coals. Thermogravimetric measures were carried out in MOM OD-103 derivatograph under the following conditions: platinum crucible, sample mass 15–100 mg, final temperature 1,000 °C, heating rate $q = 2.5$–20 K min^{-1}, atmosphere (N_2, CO_2), gas flow rate 12 cm^3 min^{-1}.

Preparation and analysis of thermal properties of azo-preoxyesters were performed according to [7]. Preparation of polyolefin–paraffin oils mixtures, thermal decomposition in laboratory scale and TGA analysis were presented in works [9, 22].

Polyethylene waxes were obtained from particular polymers in laboratory scale (sample mass 50 g) within temperature range from ambient to 380–420 °C with different average heating rate.

Conclusions

A three-parameter model allows to describe the thermal processes carried out in non-isothermal measurements in constant heating rate by linear relation (16) within the wide range of conversion degree (α).

Two methods of correlation between parameters of the model were observed: thermodynamic and analytical expression. Number of studies showed that for the chemically defined compounds thermal decomposition proceeds according to near-equilibrium curve 2 on Fig. 1 in the sense of Eq. (12) or (19). It was shown that for low values of a_2 process occurs under conditions close to equilibrium. In this case, enthalpy of reaction can be deduced on the basis of relation a_1 versus a_2. For large values of a_2 it is not possible, but the values of $T_{\mathrm{m(calc)}}$ are close to the T_{m}.

But three-parameter equation seems to be very useful for describing of thermal decomposition of complex substances. For example, in the case of thermal decomposition polyethylene LDPE with paraffin oil, the influence of a type of oil and a method of preparation on the coefficients in Eq. (15) can be clearly observed. The introduction of oil increased the a_2 value for polyethylene, which corresponds to the decrease of the decomposition temperature in the laboratory and industrial scale. Determined values of a_2 for waxes are relatively small in comparison with original polymers, so one can conclude that physical processes (distillation of low molecular fractions and less extent of thermal decomposition) dominate.

In the case of bituminous and brown coals, the first stage of decomposition refers to drying, whereas the second one concerns with pyrolysis (similar values of parameter a_2 for N_2 and CO_2). In the case of CO_2 gasification, the third stage is also observed. It was observed that values of a_2 are generally higher for CO_2 gasification, and in addition we conclude that pyrolysis process occurs similarly in both cases (influence of N_2/CO_2 atmosphere is almost not observed). It was also proved that in every case for bituminous coals higher values of a_2 are obtained than for brown coals. It is the result of differences in their structures and composition, and thus thermal stability and reactivity.

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