Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 3, 563–574

STUDY ON KINETICS OF COMBUSTION OF BRICK-SHAPED CARBONACEOUS MATERIALS

A. Mianowski[1], *R. Bigda*[2*] *and V. Zymla*[3]

[1]Department of Inorganic Chemistry and Technology, Silesian University of Technology, Krzywoustego 6, 44-100 Gliwice, Poland
[2]Institute for Chemical Processing of Coal, Zamkowa 1, 41-803 Zabrze, Poland
[3]École Centrale Paris, Laboratoire d'Élaboration des Matériaux, 92295 Châtenay-Malabry Cedex, France

Combustion of brick-shaped carbonaceous materials (carbon deposits from coke oven, coke and electrographite) was carried out in thermobalance in static air. Analysis of kinetics of the process was carried out using both classical (Arrhenius law) and newer (three-parametric equation) methods. In classical approach two types of kinetic equations were used in calculations: differential and integral. The results obtained show that, independently on kinetic variables (α – conversion degree or m – mass of sample) used in differential equations, kinetics of combustion of brick-shaped carbonaceous materials is characterized by only one pair of Arrhenius coefficients: activation energy (E) and pre-exponential constant (A). At the same time the integral equation demonstrates distinction in relation to methods based on differential equations, generating higher activation energies and separate isokinetic effect (IE). Parallel IE shows that kinetic analysis has to encompass activation energy in connection to second coefficient, pre-exponential constant A, depending on assumptions made for kinetic equations. On the other hand three-parametric equation allows describing kinetic of combustion in alternative way using only one experimental value – initial temperature in form of point of initial oxidation (PIO) – and also offers new methods of interpretation of the process.

Keywords: *carbonaceous materials, combustion, kinetic analysis, thermogravimetry, three-parametric equation*

Introduction

By carbonaceous materials we understand natural fossil coals (brown, bituminous), anthracite coals, graphite, as well as artificial carbons (soot, carbon-graphite products, coke, coal chars, pyrolytic, vitreous and fibrous carbons, charcoal etc.), except organic materials, as wood. About efficiency of their combustion decides – beside physicochemical properties (grain-size, porosity, content of individual chemical elements) – the quantity and quality of oxidant (content of oxygen, flow rate, stoichiometric ratios), thermodynamic state of a system, especially temperature and pressure, as well as process operating conditions (e.g. heating rate, fluidized bed or layer combustion).

Study on thermokinetics of combustion of different kind of carbonaceous materials on the basis of TG/DTG data was the subject of many works. Smith *et al.* [1] studied the kinetics of combustion of wide range of bituminous coals basing on Arrhenius equation. He distinguished four kinetic areas of combustion of bituminous coal. He also found linear dependence between both the temperature in which the combusted sample achieves 50% of mass and content of oxygen and carbon in sample. Cuesta *et al.* [2] presented results of investigations on oxidation kinetics of wide range of carbonaceous materials assuming pseudo-first order kinetics. In result of investigations the curvilinear dependence between values of ln$A$ and E was found. The authors concluded that the differences in reactivity of various carbonaceous materials in presence of oxygen depend on factors (ash content, grain-size of combusted sample, carbon crystal structure), which are independent on each other. Salvador *et al.* [3] analyzed oxidation kinetics of sulfurized petroleum cokes combusted in air assuming 1st order reaction kinetics. He affirmed that the content of sulfur does not have significant influence on combustion kinetics, while small ash content exerts strong catalytic influence. Minkina and Mianowski [4] studied kinetics of powdered graphite materials combusted in oxygen and air, assuming 0th reaction order and activation energy equal 0. They concluded that combustion of carbonaceous materials in oxygen gives larger differences in values of rate constant than combustion in air. Skowronski [5] by analyzing combustion of activated carbons affirmed that it proceeds in two stages: the rate of combustion in low temperature stage (450–550°C) is determined by the content of oxygen in carbon, while in high-temperature stage (550–850°C) there is domination of diffusion processes. Li *et al.* [6] studied combustion behavior of graphite doped with mixture of inorganic oxides. He stated that addition of oxides has catalytic effect on oxidation reaction of graphite decreasing both characteristic temperatures of the process and activation energy. Table 1 recapitulates results of some works mentioned above and others in the form of collec-

---

* Author for correspondence: bigda@ichpw.zabrze.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

tion of obtained values of activation energies. Present work concentrates on analysis of thermokinetics of combustion of carbon (graphite) deposits from coke oven chamber, as well as coke and electrographite. Samples have been prepared in form of little bricks and combusted in air.

Carbon deposition in coke oven

Coke oven chamber is high-temperature reactor where the coal coking process is carried out. The undesirable phenomenon in chamber is observed: the deposition of graphite on the ceramic lining. It is formed primarily on the chamber roof but also in charging holes area and ascension pipes. Graphite deposition on chamber lining is related to necessity of its periodical removing. Some pushing machines have special air nozzles which enable partial burning of carbon deposits during coke pushing. In some cases leaving empty chamber opened for some period of time is used – the air flow causes burning of formed deposits. However, in most cases such proceeding is insufficient. Then, deposits' removal using mechanical methods is necessary, what does not remain without influence on chamber lining.

The carbon (graphite) deposit formed in coke oven chamber consists of different carbon forms, which are pyrolytic carbon with soot and carbonized coal particles with small content of ash. The pyrolytic carbon is formed in Diels–Alder reaction and dehydrogenation of short-chain olefins obtained during thermal cracking of tar and volatile hydrocarbons from coal pyrolysis [11]. Particles of pyrolytic carbon are either formed in gaseous phase as spherical forms which diffuse towards wall or directly on wall creating layered structures. These structures are similar to the graphite with large number of defects into direction of crystal overgrowth axis (packing defect), while order in particular layers remains unchanged. Such structure is called turbostratic [12]. The form of created pyrolytic carbon depends on moisture content in coal charge into coke chamber: at 8% of moisture content, coexistence of spherical and stratified forms is observed; over 8% of moisture, only laminar structures are observed [13]. Presence of carbonized coal particles in the graphite deposit results from coal fines deposition on the coke oven chamber wall during charging [11].

Not published X-ray data of graphite deposits from coke oven chamber shows that it contains about 85% of different graphite crystallites (from turbostratic structures to well developed crystals), soot (ca. 12%), ca. 3% of chars conjugated with mineral matter and metallic inclusions [14].

Aim and scope of the work

Literature concerning the mechanism of carbon deposition as well as methods of its prevention numbers several works [15–22]. However, none of them concentrates on kinetics of combustion of carbon deposits from coke oven. The aim of the present work is to fill in this gap, the more so because the investigations on kinetics of combustion of graphite deposits seem interesting not only from kinetic point of view but also with regard on crucial technological aspect.

There were sampled deposits from two different points of coke oven chamber for analyses of combustion kinetics of graphite deposits:

- bottom part of ceiling (deposit A),
- roof (deposit B).

The combustion of carbon deposits occurs in temperatures of coking process (up to 1000°C), but in spite of this, their structure is similar to graphite. For this reason we also included in our analyses samples of both high quality blast-furnace coke (C) and electrographite (D) for comparison.

Considering fact that graphite deposits in coke oven chamber are in compact form, analyses described in present work are based on combustion of brick-shaped samples, not powdered, which are popular in standard thermogravimetric measurements.

The aim of this work is to compare combustion kinetics of carbon deposits with coke's and graphite's, using both classical and newer methods, focusing primarily on ash influence on combustion kinetics.

Table 1 Values of activation energy for combustion of powdered different carbonaceous materials available in literature

Reference	Substance	E/kJ mol^{-1}	Reaction order, n
Minkina and Mianowski [4]	Graphite materials	0	0
Serageldin and Wei-Ping Pan [7]	Subbituminous coal	6–12	1
Kök *et al*. [8]	Bituminous coal	9–14	1
Smith *et al*. [1]	Bituminous coal	4–290	–
Cuesta *et al*. [2]	Carbonaceous materials	54–237	pseudo 1
Hurt and Calo [9]	Char coal	105–180	0.6–1
Zolin *et al*. [10]	Char coals	135	–
Salvador *et al*. [3]	Petroleum coke	195–280	1

Classic kinetic models

In case of dry solid fuels we may assume that they are composed of both structural (C, H, O) and complementary elements (S, N, P) as well as mineral matter defined as ash (A^d) and, alternatively, free moisture (which is in equilibrium with atmospheric one). These issues are enough essential that while normalizing the conversion degree (α), an indispensable knowledge of both initial (m_i) and final mass (m_f) is needed. In case of total combustion of organic substance final mass can be regarded as ash. Thus, in kinetic equations more legitimate is using conversion degree expressed as:

$$\alpha = (m_i - m)/(m_i - m_f) \tag{1}$$

and approximately, when

$$m_f = m_i (A^d/100) \tag{2}$$

$$\alpha = \frac{m_i - m}{m_i}\left(1 - \frac{A^d}{100}\right)^{-1} \tag{3}$$

that is

$$\alpha = f\left(1 - \frac{m}{m_i}\right) \tag{4}$$

where $f=[1-(A^d/100)]^{-1}$.

For ash free substance $A^d=0$, $f=1$, thus only for such fuel constitution, conversion degree (α) equals relative mass loss in the range 0–1.

The classic kinetic equation was accepted for analysis:

$$\mathrm{d}\alpha/\mathrm{d}\tau = k(1-\alpha)^n \tag{5}$$

Equation (5) can be applied for both isothermal (T=const.) and dynamic conditions (q=const>0). Table 2 shows consequences of conversion degree transition into mass kinetic variables.

Validity of using reaction rate (dα/dτ), even for dynamic conditions, has source in works of Šesták *et al.* [23, 24, 26, 28], Memleev *et al.* [25], Koga *et al.* [27] and others [29]. Equations (6), (12) and (15) have their equivalents in simplified form (11), (14) and (18), thus one may establish relation resulting from Arrhenius law:

$$\ln k = \ln A - E/RT \tag{19}$$

in which reaction kinetic constant (k) is calculated in turn from pairs of equations:

- (6) and (11) – 0th order kinetics (n=0),
- (12) and (14) – fractional order kinetics (n=1/2),
- (15) and (18) – 1st order kinetics (n=1).

Selection of k as dependent variable results from fact that it is primary in relation to $g(\alpha)$ function, which has approximately 20 different forms.

Conversion degree makes possible using popular kinetic equations usually used in dynamic conditions and employed in works [2, 30–33]:

$$\ln\left[\frac{q}{T}g(\alpha)\right] = \ln A - E/RT,\ q=\text{const.} \tag{20}$$

$$\ln\left[\frac{qE}{RT^2}g(\alpha)\right] = \ln A - E/RT,\ q=\text{const.} \tag{21}$$

For the sake of Arrhenius law (19) we cannot make advantage of Eq. (21), because there is activation energy (E) on both sides.

Three-parametric equation

According to the source work [34] three-parametric equation has form:

$$\ln\alpha = a_0 - a_1/T - a_2\ln T \tag{22}$$

while coefficient a_0 vanishes when we introduce concept of relative rate of reaction [35]:

$$r = a_1 - a_2 T,\quad \text{where } r = -\frac{d\ln\alpha}{d(1/T)} \tag{23}$$

There have been reactions of type $A^{(s)} \leftrightarrow B^{(s)} + \nu C^{(g)}$ (or gaseous products only) considered until now, in particular thermal decomposition of solid substances in dy-

Table 2 The most popular kinetic equations in combustion analysis (used in present work)

Reaction order, n	Kinetic variables			
	Conversion degree, α		Mass, m	
n=0	$\mathrm{d}\alpha/\mathrm{d}\tau=k$	(6)	$-[1/(m_i-m_f)](\mathrm{d}m/\mathrm{d}\tau)=k$ when $m_f=m_i\,(A^d/100)$ then $-(\mathrm{d}m/m_i\mathrm{d}\tau)=k(1-A^d/100)=k'$ when $m_f=0$ then $-(\mathrm{d}m/m_i\mathrm{d}\tau)\approx k$	(7) (8) (9) (10) (11)
n=1/2	$\mathrm{d}\alpha/(1-\alpha)^{1/2}\mathrm{d}\tau=k$	(12)	$-[1/\sqrt{(m_i-m_f)(m-m_f)}](\mathrm{d}m/\mathrm{d}\tau)=k$ when (10), then $-(1/\sqrt{m_i m})(\mathrm{d}m/\mathrm{d}\tau)\approx k$	(13) (14)
n=1	$\mathrm{d}\alpha/(1-\alpha)\mathrm{d}\tau=k$	(15)	$-1/(m-m_f)(\mathrm{d}m/\mathrm{d}\tau)=k$ when (8), then $-[1/m-m_i(A^d/100)](\mathrm{d}m/\mathrm{d}\tau)=k$ when (10), then $-\mathrm{d}m/m\mathrm{d}\tau\approx k$	(16) (17) (18)

namic conditions as well chemically defined compounds – $CaC_2O_4\cdot H_2O$ [31, 35], $CaCO_3$ [34, 35], $CuSO_4\cdot 5H_2O$ [31, 36, 37], $PhN(CH_3)_2\cdot HCl$ [36] – as chemically complex substances: bituminous coals [38], mesophase pitches [39] or mixtures of polyolefins with liquid paraffin [40]. Present work broadens using of three-parametric relationship (22) also in form (23) for purposes of combustion analysis.

Assuming reaction of combustion towards oxygen:

$$C^{(s)}+O_2\leftrightarrows CO_2,\ CO,\ H_2O+\text{ash}+\text{other gases} \qquad (24)$$

Equations (22) and (23) enrich results of analyses obtained by means of classic Eqs (6), (11), (12), (14), (15), (18) and (20). Considering possibility of transforming Eq. (23) into another form, which accounts linear mass loss with temperature, when q=const, dependence m *vs*. T may be presented as straight line with negative slope. Then [41]

$$r=\frac{T^2}{T-T_\mathrm{i}} \text{ or } r=T+T_\mathrm{i}+\frac{T_\mathrm{i}^2}{T-T_\mathrm{i}} \qquad (25)$$

when $T=T_\mathrm{i}$, then $\alpha=0$.

Function (25) has minimum $r_\mathrm{min}=4T_\mathrm{i}$ for $T=2T_\mathrm{i}$.

For initial temperature of considered combustion process one may take on so-called point of initial oxidation PIO [42, 43] that is temperature in which evident start of mass loss occurs on TG curve as a result of exothermic process (combustion). In further considerations temperature T_i means PIO.

Straight line (23) intersects curve (25) in two points, so it makes secant within the range $T_\mathrm{i}<T_\mathrm{I,II}<2T_\mathrm{i}$ ($2T_\mathrm{i}$ is temperature, in which function (25) reaches minimum), where T_I and T_II are common temperatures of both relationships (23) and (25):

$$T_\mathrm{I,II}=\left(\frac{a_1+a_2T_\mathrm{i}\pm\sqrt{\Delta}}{2(1+a_2)}\right) \qquad (26)$$

where

$$\Delta=(\alpha_1+a_2T_\mathrm{i})^2-4T_\mathrm{i}a_1(1+a_2) \qquad (27)$$

Equation of the secant may be written down in form of determinant:

$$\begin{bmatrix} \boldsymbol{T} & \boldsymbol{r} & 1 \\ T_\mathrm{I} & r_\mathrm{I} & 1 \\ T_\mathrm{II} & r_\mathrm{II} & 1 \end{bmatrix}=0 \qquad (28)$$

or, after transformation, presenting other form of Eq. (23):

$$r=\frac{r_\mathrm{II}-r_\mathrm{I}}{T_\mathrm{II}-T_\mathrm{I}}T+\frac{r_\mathrm{I}T_\mathrm{II}-r_\mathrm{II}T_\mathrm{I}}{T_\mathrm{II}-T_\mathrm{I}} \qquad (29)$$

where corresponding coordinates for T_I and T_II are r_I and r_II, respectively. There was no case in experimental investigations that linear Eq. (23) was tangent to the curve (25).

Experimental

Four samples: carbon deposits from two different points of coke oven chamber (samples A and B), blast furnace coke (sample C) and electrographite (sample C) were combusted. Brick-shaped samples, weighing ca. 0.5 g each, carved out from larger pieces of material, were put into ceramic crucible with gapped sides (Fig. 1) in LINSEIS L8500 thermobalance. Next, the samples were heated in air with constant rate of 30 K min^{-1}. When mass loss has begun, heating rate started decreasing to constant value (q≈5 K min^{-1}), what made possible thermogravimetric curves accurate recording. In this stage of combustion, heating rate (calculated from linear approximation of temperature profile – Fig. 2) was equal to 2.1–7.0 K min^{-1}, depending on sample. There are fractional heating rates presented. The reason of this fact is some inertia of furnace thermocouple, which gives non ideal linear relationships T *vs.* τ for range of TG curve corresponding to mass loss analyzed. Eventually, our investigations concerns stage of the process, where q=const.

Samples were combusted in open quartz tube with atmospheric air access without forced gas flow (Fig. 3). TG measurement was conducted three times for each sample. Mass loss *vs*. time was recorded during measurement. There are both TG curves and temperature profiles presented on Fig. 4 and samples properties in Table 3.

Results

Classic kinetic models

Results of kinetic analyses are presented in function scales according to relation (19) by substituting val-

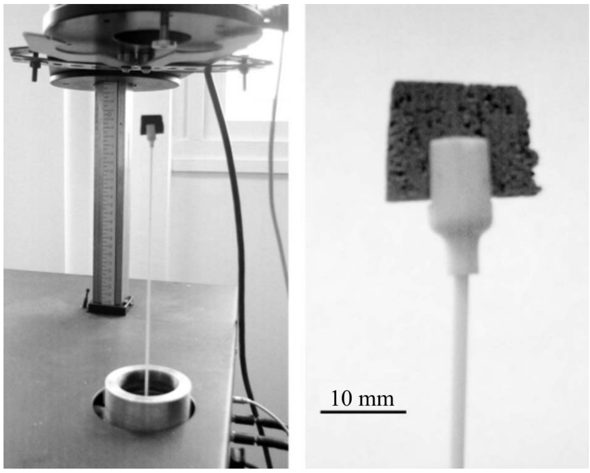


Fig. 1 View of brick-shaped sample of carbon deposit put into ceramic crucible

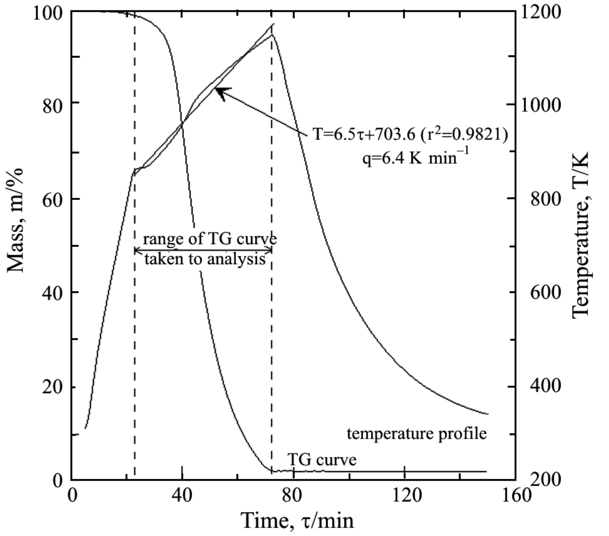


Fig. 2 The way of heating rate determination from temperature profile. We can see that linear (r^2>0.98) segment of temperature profile (q=const.) corresponds to sample mass loss during combustion

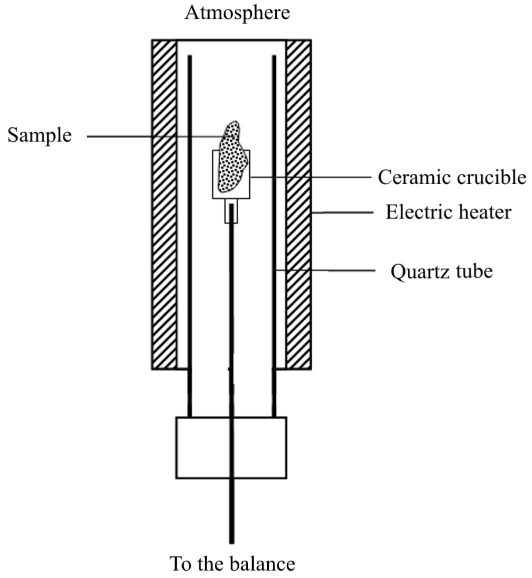


Fig. 3 Scheme of LINSEIS L8500 thermobalance used in analyses

ues determined from Eqs (6), (11), (12), (14), (15), (18) and (20) for kinetic constant k; Figs 5a–d represents it graphically. Arrangement distinction of experimental data, which result from integral form (20), in relation to other data, clearly follows from Fig. 5.

Subsequently, the results were used twice. In the first case values of kinetic parameters were determined from straight-line segments of kinetic relationships in ranges 0.02<α<0.98 for each sample separately; in some cases straight-line segment covered range 0.2<α<0.5 only. However, the aim was to determination coefficient (r^2) of the segments be at least 0.98. Figure 6 presents results in isokinetic effect (IE) coordinate system. It represents IE (30) for all analyzed samples (4×3) combusted with different heating rates and for variable kinetic models. IE may be presented in general form:

$$\ln A = E / RT_{\mathrm{iso}} + \ln k_{\mathrm{iso}},\ q=\text{const} \qquad (30)$$

There were linear relationship obtained contrary to work [2]. Surprisingly, the relationship embraced also negative values of activation energy (E) in case of coke (C). Figure 6 suggests that other data grouping should be done in spite of high determination coefficient r^2=0.9837.

At the second attempt there were values of kinetic parameters determined from straight-line segments of averaged kinetic curves (straight-lines on Fig. 5). Eight points forming two separate IE straight-lines (Fig. 7) were obtained in this way, for differential Eqs (6), (11), (12), (14), (15), (18) and for integral form (20) separately. The form (20) is less popular than (21), but according to considerations presented in work [30] it may be deemed as most valid for dynamic conditions. However, it should be emphasized that from Figs 6 and 7 we obtain isokinetic temperature T_{iso}=1202.8 K ($1/RT_{\mathrm{iso}}$=0.0001), i.e. out of range analyzed. Three straight-lines from Figs 6 and 7 (I and II) differ in abso-

Table 3 Physico-chemical properties of analyzed samples

Substance	Sample	Mass of sample, m_i/mg	Heating rate, q/K min^{-1}	Total moisture/ %	A^d/ %	V^{daf}/ %	C^d/ %	H^d/ %	N^d/ %
Carbon deposit A	A1	524	6.5	0.7	1.3	1.2	97.33	0.52	0.78
	A2	587	3.1						
	A3	602	2.9						
Carbon deposit B	B1	444	2.3	0.3	0.5	0.9	99.10	0.57	0.32
	B2	491	6.1						
	B3	504	3.2						
Blast furnace coke	C1	433	5.5	4.7	8.6	0.8	98.99	0.45	0.55
	C2	590	2.1						
	C3	608	5.6						
Electrographite	D1	509	3.0	0.8	0.2	trace	99.31	0.37	–
	D2	554	2.7						
	D3	616	7.0						

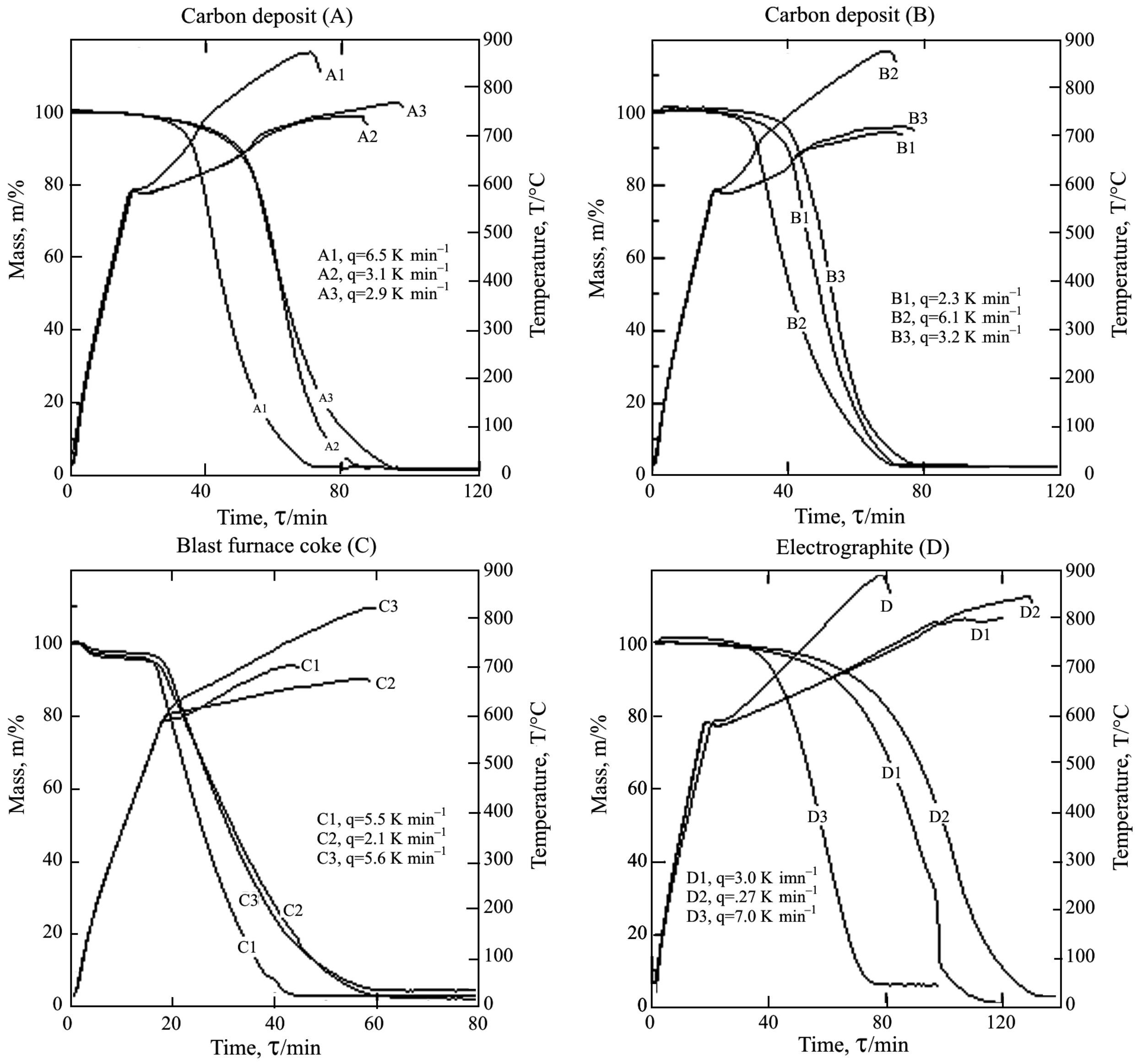


Fig. 4 TG curves (bold line) and temperature profiles (thin lines) in relation to time for analyzed samples. In order to graphs be clear the temperature profile curves are cut in point, where cooling of samples begins

lute term only, i.e. $\ln k_{\text{iso}}$. As a rule, isokinetic temperature T_{iso} in dynamic conditions is equal to temperature of maximal reaction rate T_{m}, when source of IE is mathematic formalism, i.e. factor C of the 1st type acc. [29]. It turns out that this connectivity does not occur in analyzed case of combustion and values of T_{m} run from 850 K (sample C) to 1130 K (sample D), so the following relation occurs: $T_{\text{m}}<T_{\text{iso}}$. In this case IE results from chemical similarity of substrates and it is caused by factor A acc. [29]. Generally, it is assumed that decreasing of activation energy (E), e.g. as a result of catalytic influence or insignificantly diverse chemical constitution, causes increasing of reaction rate constant. The situation occurs when temperature of reaction is lower than isokinetic one, that is: $T<T_{\text{iso}}$. Using both Arrhenius law (19) for higher (index 1) and lower temperature (index 2) and Eq. (30) twice, we obtain formula:

$$k_2 = k_1 \exp\left[\frac{E_1 - E_2}{R}\left(\frac{1}{T} - \frac{T}{T_{\text{iso}}}\right)\right] \qquad (31)$$

for $E_2<E_1$, $A_2<A_1$ and T=var.

Reaction rate constants fulfill condition $k_2>k_1$ in Eq. (33), only when $T<T_{\text{iso}}$. When $T=T_{\text{iso}}$, then $k_2=k_1$ and finally, when $T>T_{\text{iso}}$, then $k_2<k_1$. In latter case decreasing of activation energy is accompanied by decreasing of rate constant k_2.

Existence of IE of points to necessity of using activation energy (E) together with second factor of Arrhenius law, i.e. pre-exponential constant (A). It is crucial, particularly when we obtain very high values of activation energy, like on Fig. 6 (E=500 kJ mol^{-1}), exceeding literature data (Table 1).

There is one more condition appearing in experimental material analyzed, which is explicitly illustrated on Fig. 6. Namely, what assumptions are made during formulation of kinetic equations? Figure 7 also proves existence of parallel IE differing in lnk_{iso}, which is dependent on assumed both differential and integral kinetic equations. IE may be explained by many causes [29, 30, 44–51]. Using activation energy is only partly justified in this situation, and determination of activation of the samples according to criterion $T_{0.5}$ (Table 4) is more legitimate, what corresponds with common knowledge about relation between reactivity of carbonaceous materials in presence of oxygen and degree of graphitization.

Analysis of IE (30) (Figs 6 and 7) makes possible more detailed evaluation of experimental data presented on Fig. 5. Integral Eq. (20) for n=0, 1/2 and 1 clearly differs from differential Eqs (6), (11), (12), (14), (15) and (18), concretely it is characterized by lower logarithm of pre-exponential constant (ln$A$) and makes separate IE parallel to previous one.

Analysis of relationship in coordinate system ln$k$ vs. 1/T (Fig. 5) allows to state the fact of existence of common straight-line dependence (separately for both differential and integral equations) in temperature range corresponding to α=0.3–0.8 (deposits A and B) and α=0.2–0.95 (coke C), for common

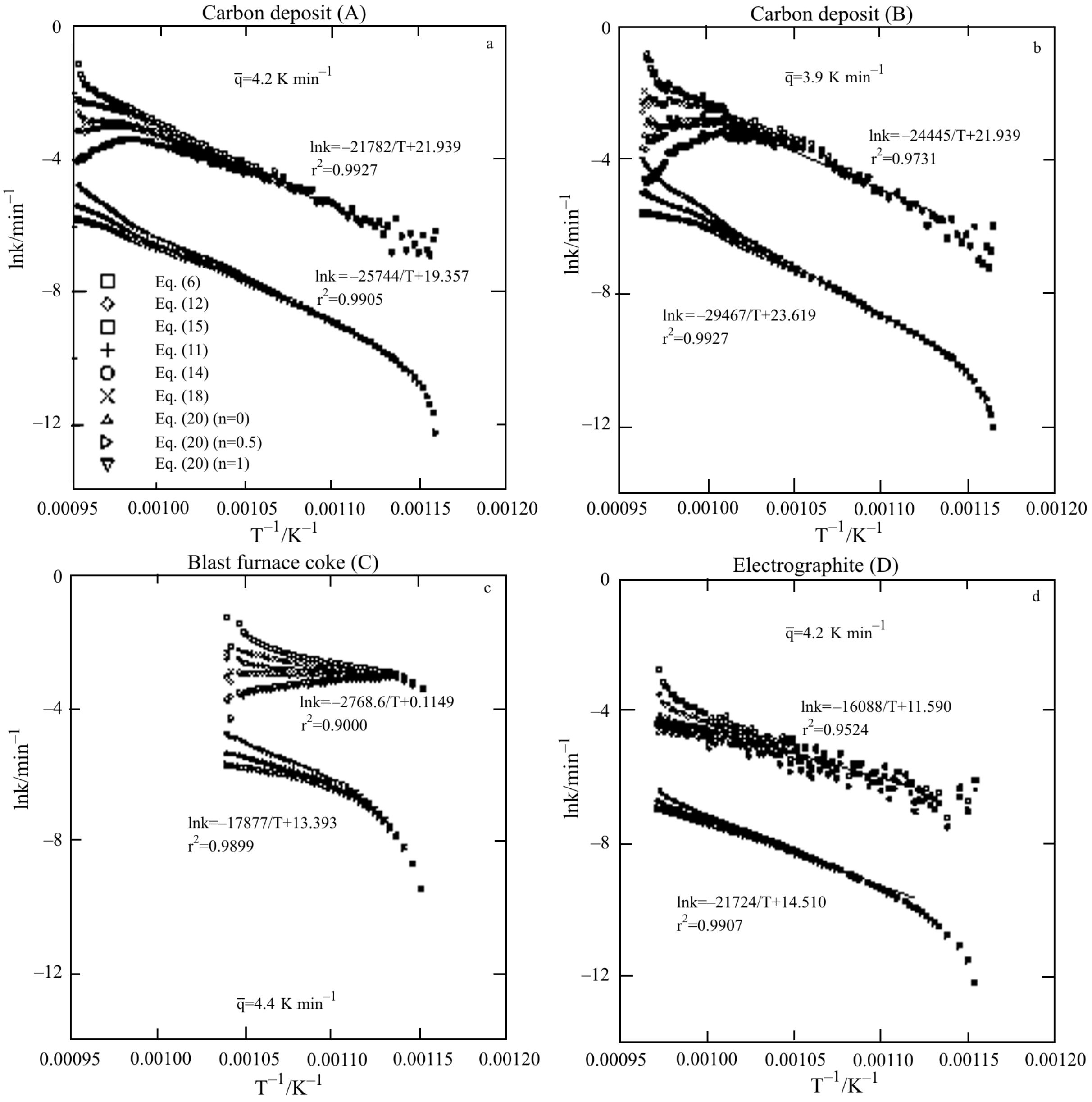


Fig. 5 Comparison of averaged kinetic curves for analyzed carbonaceous materials

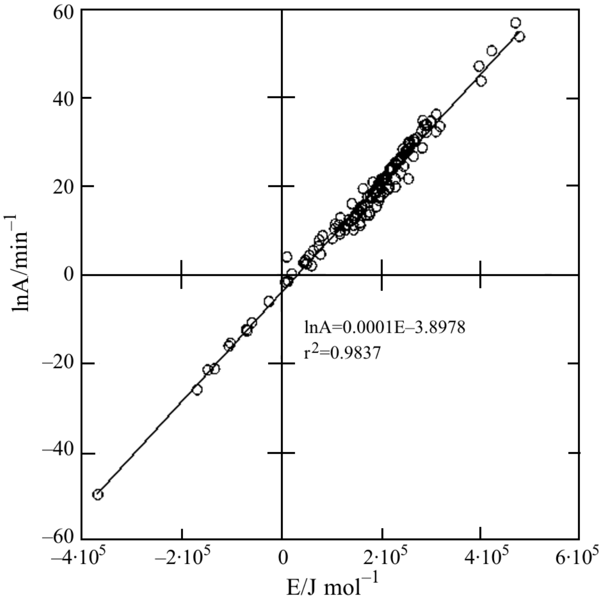
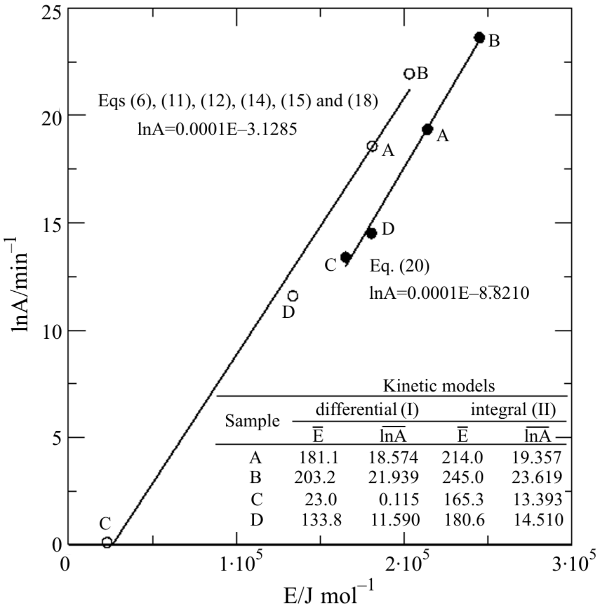


Fig. 6 Summary IE for 4×3 analyzed samples, which was obtained with use of kinetic parameters from Eqs (6), (11), (12), (14), (15), (18) and (20) (N=118 points)



Kinetic models

Sample	differential (I)		integral (II)	
	$\overline{E}$	$\overline{\ln A}$	$\overline{E}$	$\overline{\ln A}$
A	181.1	18.574	214.0	19.357
B	203.2	21.939	245.0	23.619
C	23.0	0.115	165.3	13.393
D	133.8	11.590	180.6	14.510

Fig. 7 IE for averaged values of kinetic parameters for differential relationships (6), (11), (12), (14), (15) and (18) (straight-line I), as well as for integral one (20) (straight-line II); $\overline{E}$ in kJ mol^{-1}, $\overline{A}$ in min^{-1}

Table 4 Temperatures, in which 50% of analyzed sample is combusted (averaged values)

Sample	$T_{0.5}$/K
Blast furnace coke	921
Carbon deposit B	979
Carbon deposit A	1007
Electrographite	1026

straight-line segment, what makes possible determination of single pair of kinetic parameters (E and ln$A$) independently on reaction order. From analysis of Fig. 6 follows one more interesting fact. Namely, value of activation energy resulting from averaged straight-line is very low in the case of coke sample. Thus, one may affirm that combustion of coke proceeds in diffusion or prediffusion area, where E=0 or E≈0.This fact is mentioned in some works [52, 53] and in handbook of combustion [54]. Besides, one may observe in low temperatures fragmentary kinetic area, which in case of other samples is dominating.

Three-parametric equation

Presentation of experimental data in scale r *vs.* T (Fig. 8) with the use of relationships (22), (23) and (25) provides new information about combustion of analyzed samples. Analysis of Eq. (22) is presented by Table 5, from which comes adequacy of three-parametric equation for samples A, B and D. Questionable is only using considered equation for coke samples (C). This classification is based on determination coefficient values (R^2>0.98) (Table 5).

Experimental data in scale r *vs.* T, limited by curve (25), towards location of straight-line (23) with coefficients a_1 and a_2 given in Table 5, are represented by arithmetical means for particular samples within the frame of each of analyzed samples (Figs 8a–d). The linear dependence (23) was rejected in the case of coke (Fig. 8c) for sake of low value of determination coefficient R^2<0.98.

The curve (25) is non-activation temperature profile of 0th order, henceforth called TP. Experimental data spread along the TP within whole temperature range in case of coke (Fig. 8c). There is insignificant deviation of experimental data from curve (25) observed at the end of process nearby temperature T=1000 K. It is known that curve (25) is determined by one experimental quantity, i.e. temperature T_i (PIO). It means that in first approximation coke combustion is of 0th order and of zero activation energy, in other words combustion proceeds in diffusion area in dynamic conditions. These results also explain reasons of interpretation difficulties which came across during analysis of Fig. 6c (e.g. E<0).

Combustion proceeds along TP only at the beginning of the process in case of remaining samples (A, B and D). Points begin to go down the straight-line (23) together with temperature increase, starting from point I of intersection of both dependencies (23) and (25). Coordinates of point I as T_I are determined by formula (26). The described facts allow to distinguish course of process proceeding according to the 0th order kinetics

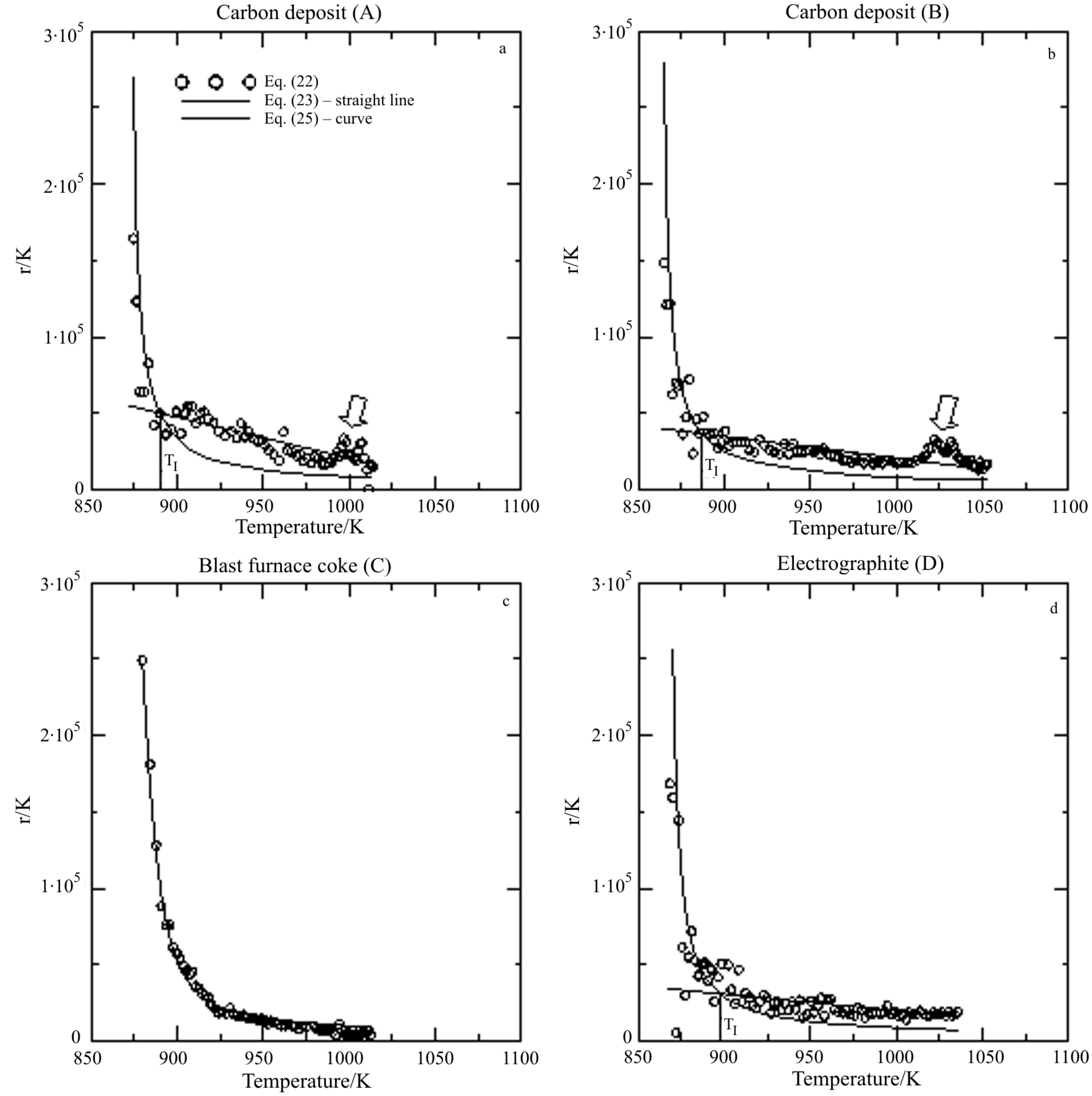


Fig. 8 Averaged values of relationship *r vs. T* (22), (23) and (25) for analyzes carbonaceous materials. The arrow points peaks showing transient increase of combustion rate

(coke, C) from 1st order process (deposits A and B and electrographite, D).

Both Fig. 8 and data in Table 5 indicate that Eqs (22) and (23) encompass most of more complicated cases (deposits and electrographite), while poorly describe simpler cases (coke) for analyzed combustion process. However, putting together mentioned equations with TP (25) make possible full interpretation of results in every case.

There is small peak observed within temperature range 1000–1020 K in case of samples of deposits (A and B). There is also very small peak nearby 1000 K observed in case of coke (C). It may be explained in following way: mass loss occurs as a result of reaction between C and O_2 during combustion of carbonaceous material, what at the same time causes increase of ash content in the sample. Ash content in relation to the rest of the sample in higher temperatures is large enough that, as a result of its catalytic influence, sudden transient increase of combustion rate take place, what is manifested by peak appearance. For the sake of large ash content in the coke sample (C) – ca. 9% – and larger possibilities of oxidizer blocking by larger amount of ash, the mentioned effect extends on whole process and it is not visible in the form of clear peak. There is no peak presence in the case of electrographite (D).

Table 5 Values of coefficients of three-parametric Eq. (22) for analyzed samples, P=0.0000

Sample	a_0	a_1	a_2	R^2
A1	1009.2	145711	125.2	0.9915
A2	1247.9	175694	155.3	0.9821
A3	1271.5	177044	158.5	0.9825
B1	5708.7	724444	721.5	0.9822
B2	1233.5	171730	153.9	0.9917
B3	1330.8	188613	165.3	0.9909
C1	3929.0	474653	500.2	0.9036
C2	11321.6	1349600	1444.1	0.9298
C3	1843.9	240305	232.2	0.9460
D1	1256.8	174613	156.8	0.9857
D2	593.7	92374	72.8	0.9879
D3	822.2	123109	101.5	0.9896

Table 6 Temperatures of straight-line (23) and curve (25) intersection, as well as PIO values for particular samples

Sample	T_I/K	T_{II}/K	T_i=PIO/K
A1	871	1123	866
A2	869	1095	865
A3	859	1090	855
B1	896	990	894
B2	865	1078	861
B3	860	1098	856
C1	867	924	865
C2	863	921	862
C3	865	1003	862
D1	869	1090	865
D2	860	1195	853
D3	884	1160	878

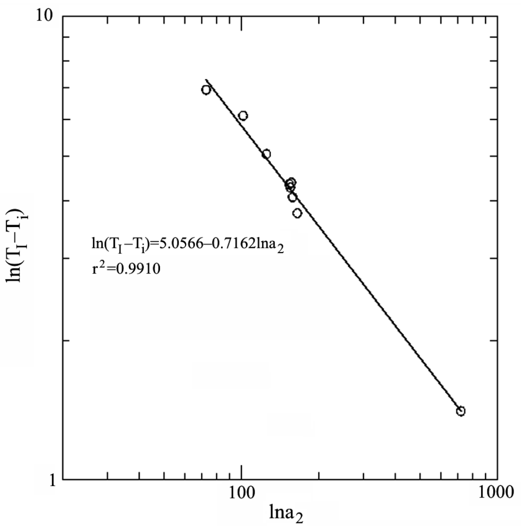


Fig. 9 Linear relationship $\ln(T_I–T_i)$ *vs.* $\ln a_2$

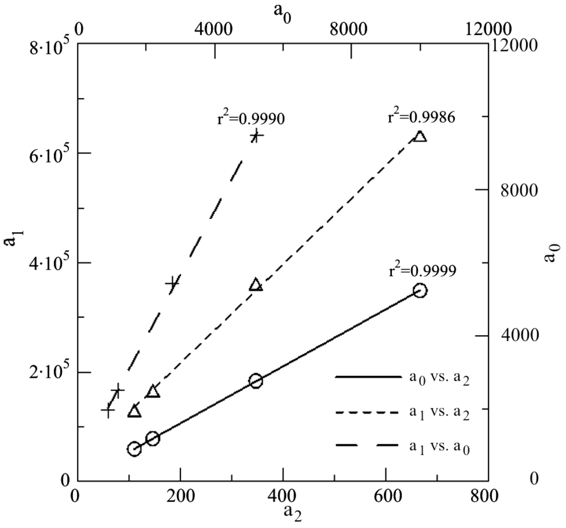


Fig. 10 Linear correlations between coefficients of three-parametric Eq. (22)

Further analyses showed existence of interesting dependence. Namely, using following values: temperature corresponding to point of intersection of relationships (23) and (25) (T_I – Table 6), PIO and coefficient a_2 from three-parametric Eq. (22) (Table 5), one may notice significant correlation between both difference $\Delta T=T_I–T_i$ and a_2 in exponential form with negative exponent in double logarithmic scale (Fig. 9). Angle between straight-line (23) and temperature axis increases together with ΔT decreasing; then $a_2 \rightarrow \infty$. In other words, while a_2 increases then thermal process is characterized by higher dynamics. On the contrary, when $\Delta T \rightarrow \infty$, then $a_2 \rightarrow 0$ and r=const.

Figure 9 broadens the possibility of treating coefficient a_2 as important tool in interpretation of thermal dynamic processes, as well exo- as endothermic ones. The results of previous analyses [36, 40] of thermal decomposition of chemical compounds and mixtures were confirmed: there is linear relationship with positive slope between coefficients of Eq. (22) a_0, a_1 and a_2 (Fig. 10). Matrix of correlation coefficients of linear relationships between constants of Eq. (22) is composed of elements with values r_2>0.99 (for diagonal equal to 1). Thus, it is sufficient to use value a_2 only, which demonstrates criterional character.

Conclusions

Technological

Coking of coal blend in typical coke oven ends in temperature ca. 1000°C. In this temperature also carbon deposits are formed. With regard to the temperature of forming we should expect similar reactivity of both coke and deposit. But analyses clearly suggest similarities between carbon deposits and electrographite, in spite of the fact that they are formed in different temperatures (ca. 1000 and ca. 3000°C, respectively). Main difference between coke and deposits and electrographite is ash content, which has catalytic influence on combustion rate (alkali compounds).

In case of deposits there is unexpected increase of combustion rate at ca. 700°C, what is presented in form of peak on curve *r vs. T* (Fig. 8). The increase is connected with sudden catalytic influence of ash components. Therefore, during deposit burning off there is no necessity exceeding combustion temperatures over 700–800°C. The temperature may depend on amount of oxidizer (air or oxygen in nozzles) and its flow rate.

Thermokinetic – classic methods

Analysis of combustion of brick-shaped carbonaceous materials (carbon deposits, coke, electrographite) in dynamic conditions shows, using classic Arrhenius law (19) expressed by differential forms independently on kinetic variable (α or m) accepted in kinetic equations, for order n=0*,* 1/2 and 1, within the range $0.3<\alpha<0.8$, that kinetics of combustion is characterized by only one pair of Arrhenius coefficients: activation energy (E) and pre-exponential constant (A) determined from straight-line segment of relationship ln$k$ *vs.* 1/T.

Determination of Arrhenius law's (19) constants from integral equations is possible only for Eq. (20), which is less popular in thermokinetic considerations than Eq. (21) and it demonstrates its distinction in relation to methods based on differential equations, generating higher activation energies with reference to other methods (Fig. 7).

Both experimental data averaging and narrowing temperature ranges down to corresponding values $0.3<\alpha<0.8$ made possible assigning of wide range of data to points characterizing particular samples by pairs of kinetic parameters, E and A. IE results from kinetic similarity and does not depend on assumed functions $g(\alpha)$. It means that each pair (E and A) is characteristic of each sample. IE (Fig. 7) means that kinetic analysis has to encompass activation energy in connection to second coefficient, pre-exponential constant, A, depending on assumptions made for kinetic equations about what parallel IE tells.

The parallel IE shows the differences between integral and differential kinetic parameters, which form two IE's, differing in isokinetic temperature T_{iso}, which was lower from T_{f} for all samples. Thus, we can conclude that decrease of E value means increase of k acc. Eq. (31). The results are uniform on that score.

In order to determine the reactivity of analyzed brick-shaped carbonaceous materials towards O_2 one propose to use value $T_{0.5}$ (temperature, in which analyzed sample achieve degree of conversion α=0.5) instead values of both activation energy E and pre-exponential constant A.

Thermokinetic – newer methods

Three-parametric equation (22) describes very well combustion processes proceeded in kinetic area (high value of $R^2>0.98$ for samples A, B and D), while it is not applicable to description of processes proceeding in diffusion area ($R^2<0.98$ – sample C).

Associating three-parametric relationship in form (25) with straight-line form (23) causes that combustion process is described by two mutually complement mathematic models of which argument is temperature, except that for determining TP only experimental value of T_{i} in form of PIO is necessary.

In case of coke (C) there was not straight line (23) observed in contrary to other samples. Coke combustion proceeds in whole temperature range along non-activation temperature profile of 0th order (TP). Comparing this fact with results of classic kinetics one may say that TP describes thermal process proceeding in diffusion or prediffusion area.

Existence of significant correlation ($r^2>0.98$) between both difference $\Delta T=T_{\mathrm{l}}-T_{\mathrm{i}}$ and value of coefficient a_2 in form of exponential relationship with negative exponent was found. When process proceeds with higher dynamics, then straight-line (23) inclination towards temperature axis increases and ΔT value decreases, what implies higher value of a_2 (Fig. 9). It broadens possibilty of coefficient a_2 treating as important tool in interpretation of thermal dynamic processes, as well exo- as endothermic.

Nomenclature

a_0, a_1, a_2	coefficients of three-parametric Eq. (22)
A	pre-exponential constant in Arrhenius equation (min^{-1})
A^{d}	ash content in dry sample (%)
α	conversion degree, $0\leq\alpha\leq1$
E	activation energy ($\mathrm{J\ mol}^{-1}$)
$\overline{E}$	averaged activation energy ($\mathrm{J\ mol}^{-1}$) – Fig. 6
f	correction factor with regard to ash content in Eq. (4)
$f(\alpha)$	function representing mechanism
$g(\alpha)$	mass integral
IE	isokinetic effect
k	rate constant (min^{-1})
k'	rate constant corrected with regard to ash content Eq. (9) (min^{-1})
$\overline{\ln A}$	averaged pre-exponential constant in Arrhenius equation (A in min^{-1}) – Fig. 7
m	mass of sample (mg),
n	reaction order, n=0,1/2 or 1
N	number of data
ν	stoichiometric coefficient
P	significance level
q	heating rate ($\mathrm{K\ min}^{-1}$)
$\overline{q}$	averaged value of heating rate ($\mathrm{K\ min}^{-1}$) – Fig. 4

r	relative rate of reaction (K)
R	gas constant (8.314 J mol^{-1} K^{-1})
r^2, R^2	determination coefficient for the linear and multiple regression, respectively; $0\leq r^2$, $R^2\leq 1$
T	temperature (K)
T_i=PIO	point of initial oxidation (K)
τ	time (min)
V^{daf}	volatile matter in dry ash free sample (%)

Subscripts

0.5	point in which α=0.5
1	larger value for E and A
2	smaller value for E and A
f	final state
i	initial state
I, II	points of intersection of relationships (23) and (25)
iso	isokinetic point.

Superscripts

(s), (g)	solid- and gaseous-state, respectively

References

1 S. E. Smith, R. C. Neavel, E. J. Hippo and R. N. Miller, Fuel, 60 (1981) 458.
2 A. Cuesta, A. Martinez-Alonso and J. M. D. Tascon, Energy Fuels, 7 (1993) 1141.
3 S. Salvador, J.-M. Commandre and B. R. Stanmore, Fuel, 82 (2003) 715.
4 M. Minkina and A. Mianowski, J. Therm. Anal. Cal., 60 (2000) 85.
5 J. M. Skowronski, J. Thermal Anal., 16 (1979) 461.
6 L. Li, Z.-C. Tan, S.-H. Meng, S.-D. Wang and D.-Y. Wu, J. Therm. Anal. Cal., 62 (2000) 681.
7 M. A. Serageldin and Wei-Ping Pan, Thermochim. Acta, 76 (1984) 145.
8 M. V. Kök, E. Özbas, C. Hiçyilmaz and Ö. Karacan, Thermochim. Acta, 302 (1997) 125.
9 R. H. Hurt and J. M. Calo, Combust. Flame, 125 (2001) 1138.
10 A. Zolin, A. Jensen and K. Dam–Johansen, Combust. Flame, 125 (2001) 1341.
11 V. Krebs, J. F. Marêché, G. Furdin and D. Dumay, Fuel, 73 (1994) 1904.
12 K. Skoczkowski, Technologia produkcji wyrobów węglowo-grafitowych (Technology of production of carbon-graphite products), Śląskie Wydawnictwo Techniczne, Katowice 1995 (in Polish).
13 V. Krebs, G. Furdin, J. F. Marêché, D. Dumay, Fuel, 75 (1996) 979.
14 B. Jesionek and M. Mikoda, Report No. 006/2003, Central Anthracite Laboratory, ZEW Racibórz 2003, Poland (unpublished data).
15 T. Nakagawa, T. Suzuki, A. Furusawa, Y. Maeno, I. Komaki and K. Nishikawa, Fuel, 77 (1998) 1141.
16 D. B. Murphy and R. W. Caroll, Carbon, 30 (1992) 47.
17 P. Lucas and A. Marchand, Carbon, 28 (1990) 207.
18 E. A. Yakusheva, Y. V. Stepanov, N. K. Cherkasov and O. I. Stadokhina, Coke Chem. USSR, 2 (1989) 16.
19 R. Cypres, Fuel Process. Technol., 15 (1987) 1.
20 J. L. Kaae, Carbon, 23 (1985) 665.
21 B. Reznik and K. J. Huttinger, Carbon, 40 (2002) 621.
22 P. Loll, P. Delhaes and A. Pacault, Carbon, 15 (1977) 383.
23 J. Šesták, V. Šatava and W. W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
24 J. Šestak, Thermal Analysis, Thermophysical and Theoretical Thermal Analysis (Part D), Vol. XII, Amsterdam, Oxford, New York, Tokyo 1984.
25 V. Memleev, S. Bourbigot, M. Le Bras, S. Duquesne and J. Šesták, Phys. Chem. Chem. Phys., 2 (2000) 4708.
26 J. Šesták and G. Berggren, Thermochim. Acta, 3 (1971) 1.
27 N. Koga, J. Šesták and J. Málek, Thermochim. Acta, 188 (1991) 333.
28 J. Šesták and Z. Chvoj, Thermochim. Acta, 388 (2002) 427.
29 A. Mianowski and T. Radko, Polish J. Appl. Chem., 38 (1994) 395.
30 A. Mianowski, J. Therm. Anal. Cal., 74 (2003) 953.
31 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 75 (2004) 355.
32 G. W. Collett and B. Rand, Thermochim. Acta, 41 (1980) 153.
33 X. Ramis, J. M. Salla, A. Cadenato and J. M. Morancho, J. Therm. Anal. Cal., 72 (2003) 707.
34 A. Mianowski, J. Therm. Anal. Cal., 59 (2000) 747.
35 A. Mianowski, J. Therm. Anal. Cal., 63 (2001) 765.
36 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 74 (2003) 423.
37 A. Mianowski and R. Bigda, J. Therm. Anal. Cal., 74 (2003) 433.
38 A. Mianowski, Some remarks on the nature of thermogravimetric profiles of bituminous coal, Proceedings of 3rd Congress of Chemical Technology, Ed. SKK TECHEM III, Gliwice, 2000.
39 A. Mianowski, S. Błażewicz and Z. Robak, Carbon, 41 (2003) 2413.
40 A. Mianowski and T. Siudyga, J. Therm. Anal. Cal., 74 (2003) 623.
41 A. Mianowski, Przem. Chem., 82 (2003) 1307 (in Polish).
42 Y. Suzin, L. C. Buettner and C. A. LeDuc, Carbon, 37 (1999) 335.
43 P. T. Williams and A. R. Reed, J. Anal. Appl. Pyrol., 70 (2003) 563.
44 A. Mianowski and T. Radko, Thermochim. Acta, 247 (1994) 389.
45 J. Pysiak and B. Sabalski, J. Thermal Anal., 17 (1979) 287.
46 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 237.
47 A. I. Lesnikovich and S. V. Levchik, J. Thermal Anal., 30 (1985) 677.
48 M. Olszak-Humienik and J. Możejko, Thermochim. Acta, 405 (2003) 171.
49 F. Tüdős and P. K. Dávid, Polym. Degrad. Stab., 50 (1995) 159.
50 J. J. Rooney, J. M. Catal., A. Chemical, 96 (1995) L1.
51 J. Straszko, M. Olszak-Humienik and J. Możejko, Inż. Chem. Proc., 1 (1995) 45 (in Polish).
52 T. Sell, S. Vyazovkin and C. A. Wight, Combust. Flame, 119 (1999) 174.
53 S. Vyazovkin, Int. J. Chem. Kinet., 28 (1996) 95.
54 S. Wójcik, Spalanie (Combustion), WNT-Warszawa 1969 (in Polish).

Received: February 25, 2005
Accepted: April 26, 2005
OnlineFirst: January 11, 2006

DOI: 10.1007/s10973-005-6973-4