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QUANTITATIVE EVALUATION AND COMPARISON OF THE THERMAL PROPERTIES OF COALS BY DIMENSIONLESS ANALYSIS

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Abstract

The $I_i = E_i/RT_i$ dimensionless evaluation is suitable for describing TG measurements according to the $E_i/RT_i = \ln A + n[\ln(1-\alpha)_i] - \ln(d\alpha/dt)_i$ equation. It is applicable for the examination of coals without any preconception like the so-called kinetic constants from the usual formal kinetic calculations. The I_i function makes the quantitative comparison of different TG measurements possible, even in case of more DTG peaks. The dimensionless analysis opens a new way for further theoretical and practical studies of the thermal properties of coals, because it characterises quantitatively the details of the processes.

Strict correlations exist also in the case of coals between the I_i functions and the constants of the compensation effect (CE). The constants of the CE ($\ln A = aE \pm b$, as slope (Tan α) and intercect) can be calculated directly from the measured data of the I_i functions for the general characterisation of the process structure.

Keywords: coal, thermogravimetry, dimensionless analysis, similarity, quantitative evaluation, compensation effect, kinetic constants.

Introduction

The supposition of the 'finger print' character of thermal analysis (TA), among others of thermogravimetric (TG) measurements induced a considerable research activity, and the formal kinetic evaluation of TG data has also been suggested very soon in relation with TG measurements of coals [1].

It is, however, a general experience in thermal analysis that both the measured data and the calculated constants of kinetic evaluations strongly depend on the conditions of the measurement, moreover on the method of calculation. The different types of diffusion or heat conduction partial processes, etc. have been considered from this aspect as 'disturbing' side–effects, consequently, numerous sophisticated measuring [e.g. 2–5] and evaluation methods [e.g. 6–15] have been developed for the elimination of

Table 1
Abbreviation of the different rate controlling models

		$f(\alpha)$	$g(\alpha)$
1	P power laws (m=1/2)	α^{1-m}	$1/m\alpha^m$
2	D	$\alpha^{1/2}$	$2\alpha^2$
3	D	α^{-1}	α^2
4	D	$2\alpha^{1/2}$	$\alpha^{1/2}$
5	D	$3\alpha^{2/3}$	$\alpha^{1/3}$
6	D	$4\alpha^{3/4}$	$\alpha^{1/4}$
7	E1 exponential law	α	$\ln \alpha$
8	B1 Prout-Tompkins	$\alpha(1-\alpha)$	$\ln [\alpha/(1-\alpha)]$
9	F1 first order	$(1-\alpha)$	$-\ln(1-\alpha)$
10	F1.5 one and half order	$(1-\alpha)^{1.5}$	$(1-\alpha)^{-1/2}-1$
11	F2 second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
12	R3 contracting volume	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$
13	R2 contracting area	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
14	Fix constant rate	1	α
15	A033 Avrami-Erofeev ($n=1/3$)	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$3/2[-\ln(1-\alpha)]^{2/3}$
16	A2 " ($n=1/2$)	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2[-\ln(1-\alpha)]^{1/2}$
17	A060 " ($n=3/5$)	$(1-\alpha)[-\ln(1-\alpha)]^{3/5}$	$5/2[-\ln(1-\alpha)]^{2/5}$
18	A3 " ($n=2/3$)	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3[-\ln(1-\alpha)]^{1/3}$
19	A4 " ($n=3/4$)	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$4[-\ln(1-\alpha)]^{1/4}$
20	D one-dimensional diff.	$1/\alpha$	$1/2\alpha^2$
21	D1 two-dimensional diff.	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
22	D2 three-dimensional diff.	$(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$3/2[1-(1-\alpha)^{1/3}]^2$
23	D3 Ginstling-Brounshtein	$[(1-\alpha)^{-1/3}-1]^{-1}$	$2/3[1-2\alpha/3-(1-\alpha)^{2/3}]$
24	Jander	$(1-\alpha)^{1/3}[-\ln(1-\alpha)]^{-1}$	$[1-(1-\alpha)^{1/3}]$

these disturbing factors from beside the 'chemical reaction'. Some of the equations suggested for the rate controlling processes are listed in *Table 1.*

The resulting experience led to an international project organised by KAMBE and GARN to standardise the conditions of the measurement and to introduce standardised materials as early as 1974 [16]. The limited efficiency of this initiative is a well-known fact.

The original purpose of TG measurements has been the direct chemical characterisation of materials. In addition, kinetic analysis has been developed for evaluation of TG data, but qualitative considerations have still remained important in the evaluation of the measurements. These qualitative considerations, however, often lead to arbitrary conclusions. It means that the direct quantitative characterisation of the examined materials by TG measurements remained unsolved.

In spite of the accurate measurements and exact calculations, it is not verifiable for example, that the second order 'mechanism' (described by *Eq.* 18 in [12]) is the characteristic 'mechanism' from among the examined nineteen other reaction rate controlling possibilities of four similar compounds [12], if all the calculated kinetic constants and each examined compound show the kinetic compensation effect (CE), and the correlation coefficient (r) of the CE is equal to 1.0000 in each case. *Fig. 1* shows some data from [12] as examples relating to the referred problem.

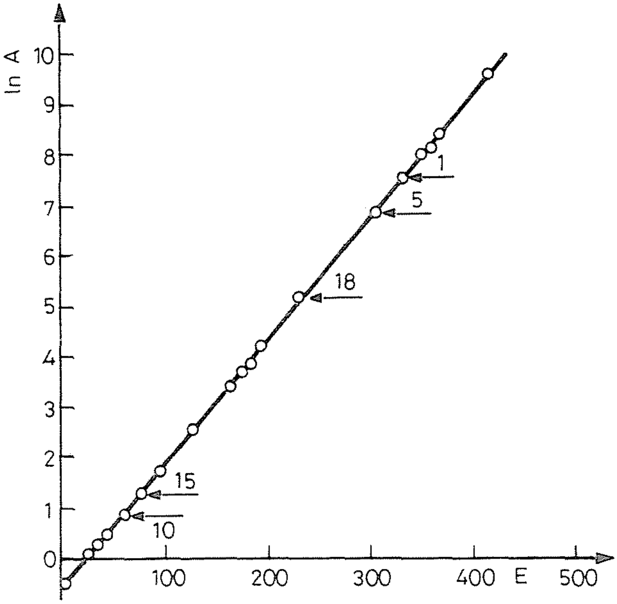

Fig. 1. Compensation effect of a thermogravimetric measurement evaluated with various differential equations [12]

Similar arbitrary, non-justified conclusions can often be found in the literature [e.g. 10, 17, 18, 19].

A further important and known fact is that different differential equations describe the thermal processes with similar accuracy. So it is arbitrary from this aspect, too, to choose one of the equations on the basis of some preconceptions.

The CE, the strictly linear relationship between the logarithm of the pre-exponential factor (ln A) and the activation energy (E) exists not only between the very different kinetic constants of one TG measurement calculated with very different differential equations but also among the different kinetic constants, measured under different conditions (laboratories).

The physicochemical origin of the CE has also been the subject of research for a long time [e.g. 14, 20], but the direct, measurable reason for the strict correlation between the kinetic constants has not yet been found.

The task to be performed is the quantitative description of TG data and quantitative comparison of different TG measurements under very different experimental conditions connected to the above mentioned problems. The results make way for the interpretation of the origin of the CE and for quantitative characterisation and comparison of different coals, as one practical application of the method.

The Dimensionless Analogy of TG Measurements

It is theoretically and practically more useful to set out directly from the measured thermogravimetric (TG), differential thermogravimetric (DTG) functions of temperature (T) and time (t), or more exactly from discrete values of the functions TG_i, DTG_i and T_i to characterise the thermal processes, instead of trying to separate the partial processes by means of different measurement and calculation methods or using preconceptions like so-called kinetic constants.

The simplest and generally used differential equation is suitable for this purpose and represents a very good tool for quantitative characterisation of the similarity of TG measurements and for looking for the effect of the factors of the measurement quantitatively [21]. It contains the Arrhenius equation as follows

$$d\alpha/dt = A\exp(-E/RT)(1-\alpha)^n, \tag{1}$$

where

$d\alpha/dt$ = rate of the thermal process,
A = pre-exponential factor
E = activation energy
n = order of reaction
$(1-\alpha)$= fraction not reacted
R = universal gas constant
T = absolute temperature.

Eq. (2) derived from *Eq.* (1) contains only the measured values of TG_i, DTG_i and T_i directly.

$$E_i/RT_i = n\ln(1-\alpha)_i \ln[1/A(d\alpha/dt)_i]. \tag{2}$$

Both sides of *Eq.* (2) are homogeneously dimensionless.

It is expedient to consider A=1 and n=1 for elimination of the preconception content of 'A' and 'n' as kinetic contants of the usual formal kinetic analysis and to preserve the dimensionless structure of *Eq.* 2 and to create tools for quantitative comparison of TG measurements. According to this, it is expedient to express the correlation among the measured data and the definition of the I_i dimensionless number by *Eqs.* 3 and 4, as follows:

$$E_i/RT_i = \ln A + n\ln(1-\alpha)_i - \ln[(d\alpha/dt)_i, \qquad (3)$$

$$I_i = E_i/RT_i. \qquad (4)$$

The I_i vs. $(1-\alpha)_i$ and I_i vs. $1/T_i$ as dimensionless functions of the concentration and temperature characterise the thermal processes.

It is expedient to muntiply both sides of *Eq.* (3) with the measured T_i or advantageously with T_iR values, denoting the I_iT_iR results as E_i. Further two functions can be calculated in this way, namely the E_i vs. $(1-\alpha)_i$ as function of the concentration and E_i vs. $1/T_i$ as function of the temperature. The last two functions can have important roles in the classification of the similarity of TG measurements.

These functions characterise the examined material and the conditions of the measurements together. They make comparison of the measurements possible, and help finding and expressing the effects of different conditions of reactions quantitatively [21].

The I_i vs. $(1-\alpha)_i$, E_i vs. $(1-\alpha)_i$ and $1/T_i$ vs. $(1-\alpha)_i$ results derived from TG measurements are shown in *Figs. 2, 3,* and *4* as examples of the application of *Eq.* (3) and comparison of the measured data. The quantities of $CaCO_3$ samples were 0.855 mg and 3460 mg in this case. (The other experimental conditions will be given later.) Although the differences between experimental conditions are unusually great, the possibility of the quantitative comparison follows obviously from *Figs. 2, 3* and *4*. The most important factor of the comparison is $\Delta(1/T)$ (*Figs. 3* and *4*) and in *Fig. 2* one constant difference, ΔA and a third factor, Δn seems to be important beside $\Delta(1/T)$ according to *Eq.* (3).

Calculation and Sensitivity of the Dimensionless Transformation

Quantitative comparison of different measurements and quantification of the effects of different factors lead to new results that can be applied practically in the industry and in the qualification of materials.

The examination of the similarity of TG measurements begins by choosing one measurement as a base for the transformation of another one. Then it is expedient to describe the calculated functions of I_i and E_i in polynomial form. The next step is to look for the best $\Delta(1/T), A$ and n transformation constants between the functions of the base and the measurement chosen for the similarity examination.

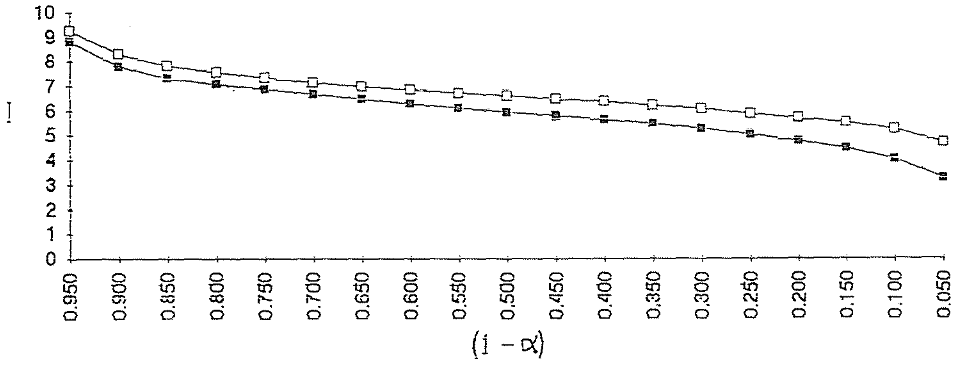

Fig. 2. *I* vs. $(1-\alpha)$ functions of 3460 mg (□) and 0.855 mg (■) $CaCO_3$ samples

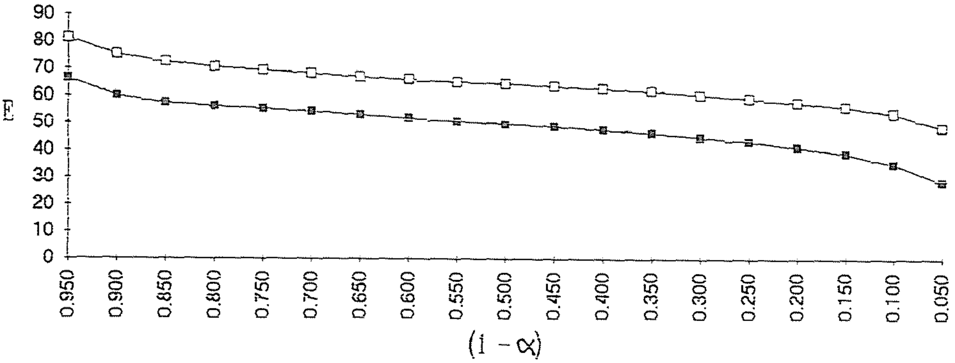

Fig. 3. *E* vs. $(1-\alpha)$ functions of 3460 mg (□) and 0.855 mg (■) $CaCO_3$ samples

The surprisingly great sensitivity of the suggested transformation method can be proved by the following results of transformation of TG data measured under extremely different conditions as follows [21].

The TG data of a 3460 mg sphere shaped marble sample were transformed onto the TG data of 0.855 mg pulverised $CaCO_3$ sample as the basis. The sample weighing 3460 mg was measured without sample holder, in air at a heating rate of 9 °C/min. On the other hand, the 0.855 mg pulverised sample was measured in Ar atmosphere, in a corundum sample holder and at a heating rate of 10 °C/min. The results of transformation are shown in *Figs. 5* and *6*.

The constants of the similarity of the two measurements are in the $(1-\alpha)_i = 0.946\text{-}0.0196$ interval with a correlation coefficient $r = 0.9986$

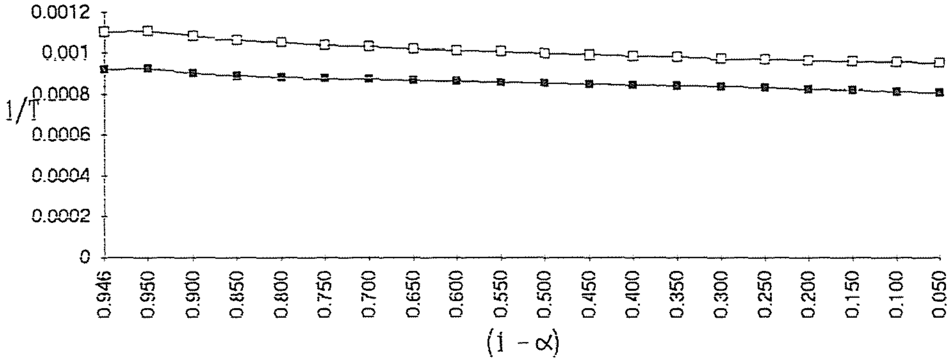

Fig. 4. $1/T$ vs. $(1-\alpha)$ functions of 3460 mg (☐) and 0.855 mg (■) $CaCO_3$ samples

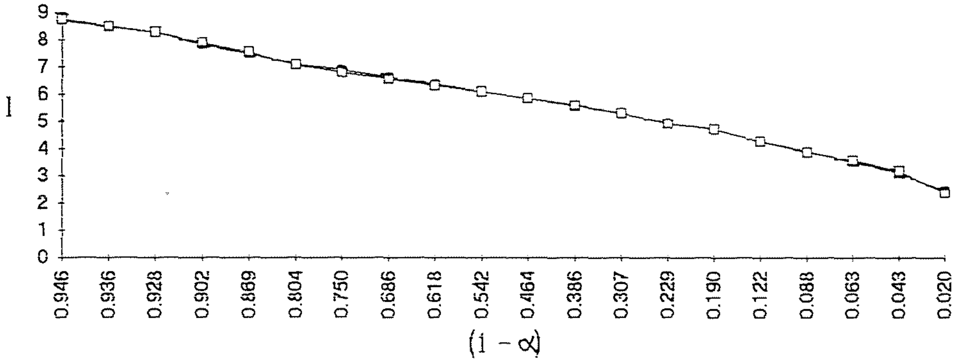

Fig. 5. I vs. $(1-\alpha)$ data of the 3460 mg $CaCO_3$ sample (■) transformed with constants $\Delta(1/T) = 1.50 \cdot 10^{-4}$, $A = 0.653$, $n = 1.33$ to the data of the 0.855 mg (☐) sample as base

as follows [21]:

$$\Delta(1/T) = 1.50 \cdot 10^{-4}, \qquad A = 0.653, \qquad n = 1.33.$$

It can be stated that the transformation can be completed with very good result in spite of the extremely different experimental conditions and in a very wide interval of the decomposition process. The meanings of the constants of the similarity are:

1. $\Delta(1/T) = 1.50 \cdot 10^{-4}$. There is a constant $\Delta(1/T)$ difference between the temperatures of the two decomposition processes (e.g. at $(1-\alpha)_i = 0.50$ decomposition the temperature of the sample weighing 3460 mg is with 166 °C higher than that of the base).

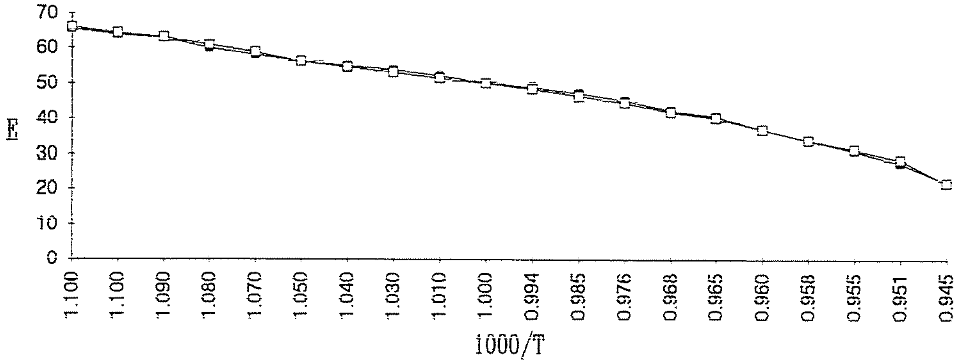

Fig. 6. E vs. $(1-\alpha)$ data of the 3460 mg $CaCO_3$ sample (■) transformed with constants $\Delta(1/T) = 1.50 \cdot 10^{-4}, A = 0.653, n = 1.33$ to the data of the 0.855 mg (☐) sample as base

2. $A = 0.653$. It means that the decomposition rate of the sample weighing 3460 mg is only 65.3% of that of the base sample during the whole process.

3. $n = 1.33$. It means that, if the $(1-\alpha)_i$ concentration or mass data of the sample weighing 3460 mg are raised to the 1.33 power, they are equivalent to the corresponding data of the base measurement.

The ratio of the sample masses in the two measurements is more than 4000. It means that, if the smaller DTG peak area is 10 cm^2, the larger is more than 4 m^2, proving the high performance and the sensitivity of the dimensionless transformation. In spite of the extremely different sample quantities and the fundamentally different experimental conditions the differences in the constants of transformation are only 3–5% by changing the base function of the two measurements.

It has to be emphasized that this dimensionless analysis makes the quantitative comparison of the *dynamic thermal processes* possible and in a very wide interval, while the known – and in the practice of industry indispensable – dimensionless analogies are applicable for comparing *stationary processes* only [21].

It is a well-known fact that there are industrial, environmental, and qualification problems related to fly ash deposits of power stations. A further industrial example is about the applicability of the 'I_i' functions to TG measurements on mixtures of fly ash and cold water which proved a self-hardening activity of fly ashes, beyond the known pozzolanic activity, but without any basic additives. The industrial and environmental protection costs may be reduced by utilizing this self-hardening activity, which could only be recognized by the help of dimensionless analysis [22].

The DTG curves have more overlapping peaks in this case. The dimensionless analysis could be applied and proved to be very sensitive independently of the number of DTG peaks.

A General Explanation of the Compensation Effect

Not only the chemical composition, but various physical, among others structural factors are changing continuously during the thermal decomposition [e.g. 4]. It is impossible today to measure all the data for the exact description and calculation of the superimposed partial processes of the decomposition, particularly in the case of solid materials. It follows from the data in *Table 1* that any attempt to solve this problem, the calculation of the so-called kinetic constants for characterisation of the material has a hidden supposition. This supposition is that only the 'chemical' partial process has an exponential temperature dependence and disregards the temperature dependences of diffusion, heat conduction, etc. This simplification leads to the apparent contradiction revealed by the CE of the formal kinetic constants of one measurement calculated by very different equations and with similar accuracy. So the criticism is very rightful of this simplification [e.g. 23].

For solving the problem, it has to be taken into consideration that analogies exist among the component, the heat and the momentum streams in thermodynamics [e.g. 24]. It follows from this that there is an analogy among the exponential temperature dependence of the chemical processes and the different forms of diffusion [e.g. 25] and heat conduction, too, during the TG measurements. This exponential temperature dependence of the different chemical and physical partial processes is proved by the dimensionless analysis [21]. This is the basis of the great sensitivity and transformability of the I_i functions (*Figs. 5* and *6*) and it makes the elucidation of the connection between the measured data and the CE possible as it has been introduced and applied recently [27] and as it is repeated shortly as follows.

The usual form of the CE is *Eq.* (5).

$$\ln A = a \cdot E \pm b. \tag{5}$$

Eq. (6) shows the properly regrouped *Eq.* (3) with the average values of the measurements for comparison to *Eq.* (5)

$$\ln A \cong \overline{(1/RT_i)} \cdot \overline{E_i} - \overline{n \ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}. \tag{6}$$

Consequently the 'a' as the tan α of the CE is

$$a \cong \overline{1/RT_i} \tag{7}$$

and 'b' as the intercept of the CE is

$$b \cong -\overline{n\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}. \tag{8}$$

One part of *Table 2* shows the constants of the CE calculated with the average data of the I_i functions, i.e. with the measured data directly and without any preconception.

It is ascertainable that the slope $\overline{1/RT_i}$ shows the general temperature dependence and the intercept $\overline{-n\ln(1-\alpha)_i} + \overline{\ln(d\alpha/dt)_i}$ shows the general structure dependence of the thermal process. It is obvious that the value of the average $\overline{E}$ calculated by *Eq.* (6) has a different meaning from that of the usual idea of the activation energy in the literature. According to this it is justified to introduce the idea of the 'general activation energy' for this average $\overline{E}$ because it characterises the total process and not only the 'chemical' part.

The reliability of these results is demonstrated also in *Table 2* by leaving out each third from the discrete points of measurement, decreasing their number from 20 to 14.

The experimental conditions influence the thermal process through the different partial processes, but the character of the system does not change fundamentally during the decomposition. Consequently, *the I_i functions show the details of the partial processes of the different measurements and the CE characterises the status of the examined system generally.*

The data in *Table 2* prove these conclusions by comparing the constants of the CE with data of other origin. In addition, *Table 2* shows the trend of the dependence of tan α $(\overline{1/RT_i})$ on the examined materials and – as examples – the measured data were completed by data from the literature, too [22, 26–29].

These experiences and results about the CE together with the I_i functions can open up a new way for the quantitative characterisation and comparison of coals like raw materials and different products, opening a new field for the application of TG measurements.

Evaluation of TG Data of Coals by I_i Functions

The scope of any systematic description of coals is seriously limited by their large chemical and structural variability. According to this, the widely different industrial applications of different types of coals induced also various qualification methods. Beside the proximate and ultimate analysis, a series of standardized, bench-scale and pilot plant systems for the best use of coals had to be developed and applied. This effort, however, does not

Table 2

Constants of the compensation effect of some thermal decomposition processes

		$\ln A = aE \pm b$ functions calculated with *Eq.* (6)				other	origin	
Sample name	quantity; mg	$\overline{a}$	$\overline{E_i}$	$\overline{b}$	$\overline{\tan\alpha}$	$\tan\alpha$	b	
$CaCO_3$	0.855	0.1254	51.37	−6.4442	7°09'12"	6°41'45"	−5.7217	(1)
	100	0.11976	52.32	−6.2657	6°49'45"	6°27'51"	−6.3020	(1)
	200	0.11536	54.26	−6.2596	6°34'50"	6°20'43"	−5.7839	(1)
	400	0.11265	57.69	−6.4994	6°25'39"	6°02'22"	−5.4843	(1)
	1000	0.10924	59.51	−6.5009	6°14'03"	5°51'29"	−5.6422	(1)
20 points	3460	0.10373	63.83	−6.6799	5°55'20"	5°42'18"	−5.7260	(1)
14 points	3460	0.10378	63.68	−6.6732	5°55'30"			
Kaolin (dehydration, loose sample)						8°15'22"	—	(2)
$CaC_2O_4.H_2O$(dehydration, loose sample)						13°23'34"	—	(2)
$CaC_2O_4.H_2O$(dehydration, pressed sample)						12°59'07"	—	(2)
Gypsum	first peak	0.29020	20.91	−6.0693	16°10'58"	16°10'54"	−6.6738	(4)
200 mg	second peak	0.27240	17.78	−4.8425	15°14'16"	15°14'17"	−5.9489	(4)
	usual kinetic evaluation					15°47'08"	−4.7672	(5)
$(NH_4)_2S.H_2O$ (dehydration)						19°06'40"	-	(3)

(1) CE calculated with four equations [26]
(2) CE calculated with ten equations [28]
(3) CE from [29]
(4) CE calculated with different 'n' values [22]
(5) CE calculated with eight equations, data from [30]

eliminate the importance of the empirical knowledge, because of the great number of factors known for coals. Beside these facts, the application of the dimensionless analysis is a new method for the complex characterisation of coals. The applicability of the method is demonstrated by TG measurements of three different coals. The results of the proximate and ultimate analysis of these coals are listed in *Table 3*.

The experimental conditions used in the simultaneous, non-isothermal thermogravimetric [3] measurements were as follows:

Table 3
Results of proximate and ultimate analysis of the examined coals

Measured parameter; wt %	Name of sample Lignite A	 Lignite B	 Bituminous C
Moisture	8.1	8.9	8.7
Ash	5.7	6.6	6.5
Volatile matter	37.7	39.1	36.6
Fix-carbon	42.5	45.4	48.2
Calorific value; MJ/kg	28.61	29.00	27.81
Carbon	66.2	65.2	64.3
Hydrogen	4.08	4.8	5.2
Nitrogen	1.4	1.6	0.8
Total Sulphur	0.72	0.76	0.79
Oxygen (by difference)	15.58	13.82	15.61

Sample weight: 200 mg, heating rate: 5 °C/min, type of sample holder: cylindrical Al_2O_3, purging gas: N_2 (O_2 content about 10 ppm), flow rate 40 dm^3/h.

Eq. (3) was used for evaluation of the TG_i, DTG_i and T_i data, and the calculated constants of the similarity of different coals are shown in *Table 4*, changing the base measurement of the transformation.

It follows from the constants of the transformation in *Table 4* that the similarity is good between Lignite A and Lignite B and it is not depending on which of the two has been chosen as the base of transformation, similarly to the thermal decomposition of the $CaCO_3$ as an example given above.

In spite of this, the constants of the Bituminous C depend on the base of transformation. This follows from the chemical and structural complexity of the different range of coals. The I_i vs. $(1\text{-}\alpha)_i$ functions in *Figs. 7–10* demonstrate the accuracy of the transformation and the effect of the change of the base measurement mentioned above. The accuracy as variance (s) (*Eq.* (9)) of the transformation can be calculated by the usual statistical method as follows. It is a further tool of quantitative qualification of different coals.

$$s = \sqrt{\frac{\sum_{i=1}^{n}(I_i^B - I_i^{Tr})^2}{n-1}}. \tag{9}$$

These results and the ratio as per cent of the average I_i are also given in *Table 4*.

The formal kinetic evaluation connects the TG measurements with the phenomenon of the CE. The formal kinetic constants of the examined coals listed in *Table 5* were calculated by means of *Eq.* (1) with $n = 1$. The data are completed by constants from the literature [31,32]. *Table 6* shows

Table 4

Constants of similarity of different coals by transformation of the I_i functions

	Base Lignite A	Transformed Lignite B	Base Lignite B	Transformed Lignite A
$\Delta(1/T)$	0	$9.37 \cdot 10^{-7}$	0	$-2.54 \cdot 10^{-7}$
A	1	0.84	1	1.15
n	1	0.74	1	1.22
Δ °C 50% dec.	0	0.5 °C	0	0.1 °C
s; %		0.32; 4.9%		0.15; 2.3%
	Lignite A	Bituminous C	Bituminous C	Lignite A
$\Delta(1/T)$	0	$2.66 \cdot 10^{-5}$	0	$-2.32 \cdot 10^{-5}$
A	1	0.56	1	2.58
n	1	0.60	1	1.68
Δ °C 50% dec.	0	15.8 °C	0	−3.4 °C
s; %		0.24; 3.6%		0.62; 9.2%
	Lignite B	Bituminous C	Bituminous C	Lignite B
$\Delta(1/T)$	0	$2.56 \cdot 10^{-5}$	0	$-1.91 \cdot 10^{-5}$
A	1	0.65	1	2.40
n	1	0.85	1	1.50
Δ °C 50% dec.	0	15.5 °C	0	−6.6 °C
s; %		0.25; 3.8%		0.60; 8.7 %

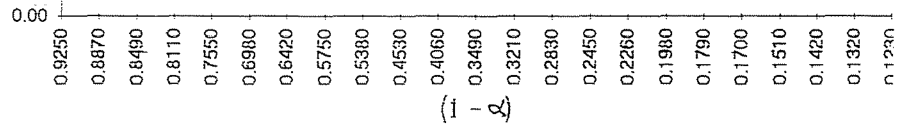

Fig. 7. *I* vs. $(1-\alpha)$ functions of Lignite A (☐) and Lignite B (■) as base of transformation

the evaluation of the TG measurements of the coals by *Eq.* (6), comparing the constants of the CE to data of other origin similarly to *Table 2*.

It follows from the results in *Tables 2, 4* and *6* that in the case of thermal decomposition of materials like $CaCO_3$, the exponential temperature dependences of the chemical, the diffusion and the heat conduction partial

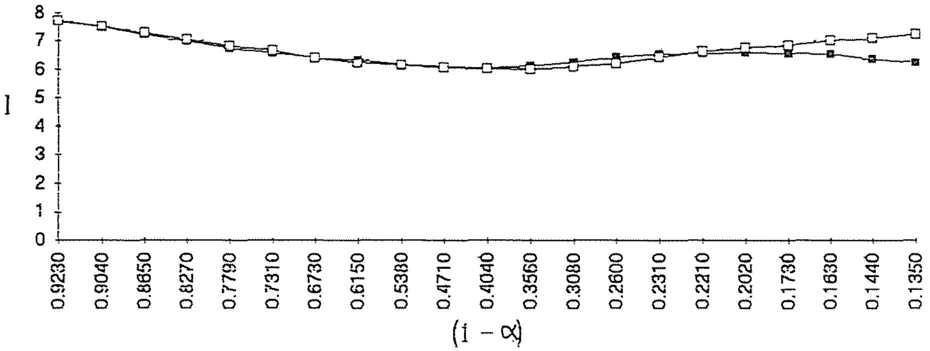

Fig. 8. I vs. $(1-\alpha)$ functions of Lignite B (☐) and Lignite A (■) as base of transformation

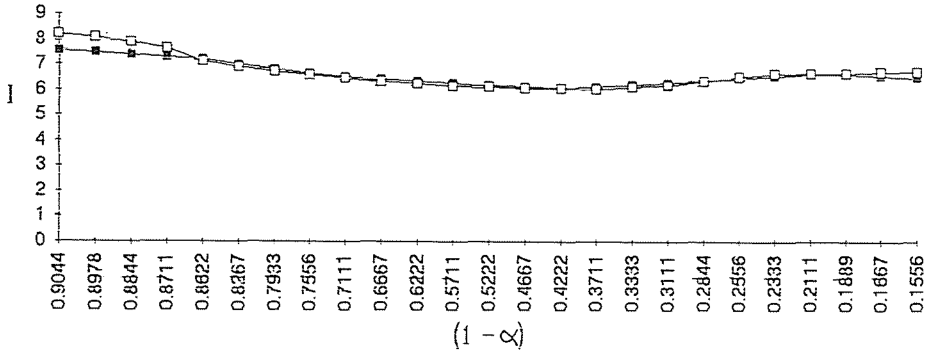

Fig. 9. I vs. $(1-\alpha)$ functions of Bituminous C (☐) and Lignite A (■) as base of transformation

processes are observable in connection with each other. In spite of this, the chemical composition and 'structure' seems to be the determinant factor in the thermal decomposition of coals, covering the importance of the physical structure.

The dimensionless evaluation of rapid and cheap dynamic TG measurements provides characteristic and quantitative information about the properties of coals. Beside this, the dimensionless analysis makes the characteristic and quantitative comparison of the different coals possible. The simple and useful possibility of the alteration of the experimental conditions opens a further new way for extending the scientific and empirical experience about the different determining factors of coals.

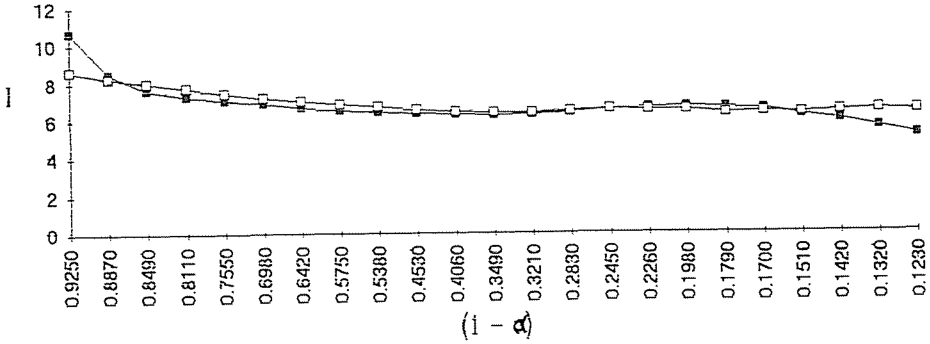

Fig. 10. I vs. $(1-\alpha)$ functions of Lignite A (□) and Bituminous C (■) as base of transformation

Table 5
Formal kinetic constants of coals

Name of sample	ln A	E, kJ/mol	Source of data
Lignite A	17.93	134.25	*Eq.* (1)
Lignite B	10.84	96.92	"
Bituminous C	4.37	63.20	"
	35.49	231.96	[31]
	33.69	228.48	[32]

Table 6
Constants of the compensation effect of the thermal decomposition processes

$\ln A = aE \pm b$ functions calculated with *Eq.* (6)						other origin	
Sample name	quantity; mg	$\overline{a}$	$\overline{E_i}$	$\overline{b}$	$\overline{\tan\alpha}$	$\tan\alpha$	b
Lignite A	200	0.1721	39.09	−6.7267	9°45'53"		
Lignite B	200	0.1743	39.45	−6.8763	9°53'15"		
Bituminous C	200	0.1744	39.48	−6.8870	9°53'43"		
CE of all kinetic constants in *Table 5* (*Eq.* (1) [30, 31])						10 °06'24"	−6.0447

The phenomenon of the base dependence of transformation in the case of coals helps to deepen the quantitative characterisation of the similarity and to provide additional information for the quantitative comparison of different coals by changing the base of transformation systematically.

The dimensionless analysis of coals (*Tables 4, 6, Figs. 7, 8, 9, 10*) directs attention to the importance of the classification of similarity examinations.

Conclusions

The application of the I_i functions, the dimensionless description and evaluation of TG measurements are a good tool for solving the contradictions of formal kinetic constants. The I_i functions can be used for quantitative characterisation and comparison of the thermal processes of coals, too, and it even makes a quantitative description of the effect of different material factors and experimental conditions possible; giving new information for industrial application and for material qualification, too.

Strict correlations exist between the I_i functions and the CE, making the explanation of the CE possible by measured data directly. The I_i functions characterise the details of the TG processes of coals, and the constants of the CE characterise the examined system generally. Among these constants, the meaning of the $\overline{E}$ as the 'general activation energy' differs from the usual idea of the activation energy. The I_i functions and the constants of the CE together are suitable for quantitative characterisation of the TG processes of coals as industrial raw materials and products.

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