Combination of Derivatograhy and Pyrolysis Methods for Prediction of Quantitative Characteristics of Carbon-Containing Materials

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ABSTRACT: 29 samples including coal precursors (C^{daf} = 44.3–59.0 %) and coals of different rank (C^{daf} = 64.1–93.7 %) have been studied using thermodestruction methods. The use of derivatography has been shown to enable differentiation of optimal pyrolysis temperature (T_{max}) for the samples with different carbon content. Pyrolysis mass balance of the samples has been calculated. Simple and multiple regressions describing the dependence of the pyrolysis tar yield (T^{daf}_{sK}) obtained at T_{max} on the carbon content (C^{daf}, %) in the sample were analyzed. It was shown that T_{max} on the DTG-curve is the temperature point conveying important information on the composition and technological characteristics of carbon materials. An intimate correlation relationship between the parameters studied (C^{daf}, T_{max}, T^{daf}_{sK}) for the coal precursors and different rank coals (*r* = 0.950–0.970) has been found.

KEY WORDS: coal precursors, different rank of coals, thermodecomposition, pyrolysis products, regression equations.

Introduction

The search for rational and effective ways of processing carbon containing materials is the burning problem of coal chemistry today. It requires determining the optimal conditions and express methods to estimate thermal transformations of carbon–containing materials at their heating. At present there are a number of well-known methods for testing coal properties and their behavior in different thermal processes. A series of coal divisions into classifications for estimation of technological parameters of coals in practice has stood the test of time. The basic of them are the genetic, industrial and industrial–genetic classifications covering all different rank coals from brown and hard coals to anthracites. Relevant information about the structure and reactivity of coals can be obtained using thermodecomposition methods. However, before a pyrolysis it should be elucidated if the chosen temperature is optimal for the rank of each examined sample and if the decomposition products obtained are primary. Their analysis can yield extensive information about the structure of coals (Shinn 1984, Krebs et al. 1984, Solomon et al. 1993, van Heek et al. 1994).

One of the above mentioned methods is a widely applied method of determination of the semi–coking products yield (Standard ISO 647-74 1987) which involves thermodecomposition (pyrolysis) of coals at 520 °C without air access with the formation of water, tar, gas and charcoal. Pyrolysis products yield is a parameter that reflects chemical nature, structure and properties of the organic mass of coals. It is one of the classifying parameters widely used in industry for estimation of the technologic characteristics of coals to ensure their more effective use in different conversion processes (Avgushevich et al. 1987, Kamneva et al. 1990, Tajtz 1983). The main disadvantage of this method is fixed pyrolysis temperature, i.e. 520 °C, which does not correspond to DTG data and cannot be extended to all different rank coals. For low rank coals (C^{daf} = 64.0–79.0 %) this temperature is too high, whereas for high rank coals (C^{daf} = 88.0–95.0 %) it is too low. Therefore this method is intended chiefly for middle rank coals (C^{daf} = 83.0–89.0 %) and it cannot be applied to coals precursors such as cellulose, lignin, wood and peat to characterize their structure and properties.

The problem of the particular components of the initial vegetable biomass, which formed coals, still remains as one of the most challenging and debatable in coal chemistry.

The use of coal precursors as additional objects of research is needed due to the following considerations:

1. There is no clear by defined scientific basic for the integration of coal precursors and coals into a uniform classification
2. There is no uniform approach in the joint investigation of coal precursors and different rank coals
3. Strict evidence of the genetic ties between coal precursors and different rank coals is needed
4. Information on chemical composition and structure of a wide series of materials ranging from coal precursors to different rank coals and their pyrolysis products can give some useful evidence on the pathways of organic mass transformation during diagenesis and coalification stages.

Herewith it is very important to carry out pyrolysis in mild operating conditions in order to except secondary decomposition reactions and cross linking reactions during semicoking and coking. Shevkoplyas and Galushko (2004) proposed a method thermodecomposition of carbon–contained materials at minimal temperature and soaking time for the keeping primary pyrolysis products in the reaction zone, which can be effective for the study of structural peculiarities of various carbon contained materials.

The aim of this paper is to explore the possibilities of using the thermal methods and elicitation of new quantitative characteristics for different rank coals and coal precursors to reflect their composition and structure at different stages of coalification, and the mathematical description of the respective statistical correspondences between the carbon content, pyrolysis temperature and tar yield in the samples under study.

No.	Coal precursors, coal mine(deposit), coal seam	Proximate analysis %				Ultimate analysis % daf		
		W^a	A^d	S_t^d	V^{daf}	C	H	O+N
1	Cellulose	5.8	0.1	–	75.0	44.3	6.4	49.3
2	Wood (pine)	7.4	0.7	–	71.5	51.6	4.9	43.5
3	Wood (poplar)	7.1	0.5	–	74.8	52.8	6.4	40.8
4	Peat	61.4	43.9	0.3	70.0	57.0	6.0	36.0
5	Peat	3.4	77.7	0.3	70.0	57.0	6.0	37.0
6	Lignin	4.6	5.2	0.1	71.0	59.0	6.2	34.8
7	Verbolozovskay	55.6	35.4	2.7	61.3	62.4	5.1	27.6
8	KWB “Belchatow”, Poland	60.1	52.9	2.7	55.4	64.1	5.0	28.2
9	Novomirgorodskay, Ukraine	42.0	25.2	2.9	63.2	65.4	6.1	28.5
10	Konstantinovskay	47.4	10.1	4.1	61.0	66.8	5.8	27.4
11	Protopopovskay	48.7	19.6	4.3	59.6	69.6	6.0	18.9
12	KWB “Turow”, Poland	51.0	4.8	3.4	59.1	71.0	4.8	21.1
13	Kansk-Achinsk, Russia	13.1	5.8	0.2	45.2	74.3	4.9	20.5
14	Trudovskay, l_4	1.4	3.2	3.2	41.0	76.6	5.6	14.6
15	Kurachovskay, l_2	1.9	5.1	5.6	43.0	76.2	5.2	13.0
16	Kurachovskay, l_4	3.0	7.2	1.0	37.0	79.0	5.1	14.9
17	Lidievskay, l_3	1.6	4.6	2.3	38.0	82.2	5.4	10.9
18	Lidievskay, l_1	1.2	3.1	1.0	35.0	82.7	5.3	11.0
19	Novator, k_5	2.1	1.5	0.7	35.4	83.5	5.4	10.4
20	Zasaydko, m_3	1.3	2.5	3.1	35.5	84.3	5.3	7.3
21	Zasaydko, k_8	0.9	2.6	4.1	30.5	85.4	5.2	5.3
22	Zasaydko, l_1	1.3	8.2	1.1	32.7	86.1	5.4	7.4
23	Komsomolets, m_2	1.6	15.2	1.2	29.5	87.4	5.3	6.1
24	Batova, k_8	2.8	8.3	3.0	22.4	88.6	4.8	3.6
25	Jasinovataja Glubokaya, l_6	1.0	7.4	1.7	21.0	88.9	4.5	4.8
26	Pravda, h_3	1.5	36.2	3.1	13.5	89.7	4.2	3.0
27	60-years of Soviet Ukraine, h_8	1.1	12.3	1.2	12.9	90.3	4.3	4.2
28	№ 20, h_8	1.9	7.4	1.7	4.0	93.6	2.3	2.4
29	Progress, h_8	3.2	5.3	1.5	4.2	93.7	1.9	2.9

■ **Tab. 1.** Characteristics of coal precursors and different rank coals.

Materials and methods

The study was carried out on the brown coals of Ukraine, Poland and Russia; besides hard coals and anthracites of Donetsk basin (C^{daf}= 65.4–93.7 %). Some species of coal precursors (C^{daf} = 44.3–59.0 %) were used: leafy and coniferous wood and its components such as the cellulose and lignin (C^{daf}= 44.3–59.0 %) and also peat containing (C^{daf}= 57.0 %), which is the primary product of biochemical transformation of both plant species and woods. Characteristics studied of carbon contained materials presents Table 1. Nomenclature data using in this paper for a study of proposed indexes illustrates Table 2.

The chemical nature of fuels can be estimated by the yield and composition of pyrolysis products only on condition that their primary decomposition products are also analyzed. The latter, however, easily undergo reactions of condensation, polymerization, isomerization, etc. being transformed into secondary products with the composition and properties largely depending on the conditions of performing the process. Therefore the pyrolysis temperature must be chosen individually for each analyzed sample in order to eliminate or minimize the influence of reactions of secondary destruction and condensation.

Differential thermogravimetric analysis (DTG) of the samples permits to determine this temperature. Besides this method that follows the changes in the mass (TG and DTG curves) and the thermal effects (DTA curves) can provide valuable information on the behavior of samples heated up to 950 °C and characterize the process at each individual temperature. In our opinion, the most important DTG data are the temperature range and maximum temperature (T_{max}) of the endoeffect, which are related to the basic thermodecomposition of carbon containing materials. By determining the location of the T_{max} it is possible to find the predicted temperature for further thermal treatment of each coal and coal precursors with different carbon content.

Differential thermal analysis was carried out in a Paulic–Paulic–Erdey Q–1500D thermobalance at the heating rate of 10 °C min^{-1} in a closed platinum crucible using the samples of 200–500 mg. The analysis of TG and DTG curves was performed with the aim to estimate T_{max}, T_b (beginning) and T_e

Characteristic	Method of determination
C^{daf}, wt %	Standard ISO 647-74
T^{daf}_{sK} – pyrolysis tars yield, wt %	Standard ISO 647-74
T_{max} – the temperature corresponding to the maximum weight loss rate	DTG analysis

Tab. 2. Nomenclature of indexes.

(end) of the basic endoeffect decomposition for all the investigated samples (Sklyar and Tutunnikov 1985).

In the study reported here pyrolysis was carried out in a fixed bed reactor (volume 20 cm^3). The 2–10 g samples crushed at ≤ 0.5 mm were heated at 25 °C min^{-1} up to T_{max} temperature (earlier defined for all the samples by DTG method) and kept at the final temperature for ten minutes. This soaking time was sufficient for complete volatilization of primary pyrolysis products from the reactionary zone (Aronov et al. 1968).

Upon the completion of pyrolysis the yield of water, tar, gas and solid residue were determined and the mass balance was calculated.

Authors (Butuzova et al. 2003, Ivanov et al. 2003, Miroshnichenko 2003, Gulmaliev et al. 2004) using mathematical statistic methods to estimate the relationship between the proximate and ultimate analyses of coals and their basic physical–chemical and technologic properties. The application of mathematical statistics models is an attractive pathway to find new valuable methods broadening our ideas about structure and technological characteristics of carbon containing materials.

In this paper quantitative description of interrelationship between experimental C^{daf}, T_{max} and T^{daf}_{sK} values has been made using of regression and correlation analyses. The pair correlation coefficient (*r*) and the standard error of estimation (S_o) were used to determine the functional dependence between the aforementioned parameters. The adequacy of regression equations was determined by the Fischer´s criteria at the level of confidence 95 % (Charykov 1984).

Results and discussion

Figs. 1 and 2 show the DTG curves in the range 20–800 °C, which characterizes the mass loss rate for coal precursors and different rank coals under investigation. On the basis of these curves, the values of T_b, T_{max} and T_e were calculated for the endoeffect corresponding to the basic decomposition region (Table 3). It is evident in Fig. 1, Fig. 2 and Table 3 that coal precursors and low rank coals have the lowest T_b, T_{max} and T_e values, and high rank coals have highest T_b, T_{max} and T_e values. The evolution of these parameters during coalification indicates that they are strongly influenced by the nature of carbon containing materials. Therefore the aforementioned temperature region is specific for each carbon containing material and reflects both the general regularities and the differences of coal structural organization at different stages of their metamorphism. The temperature maximum (T_{max}) in the DTG curves corresponding to the highest rate of mass loss for all the samples is the temperature point which separates the temperature region of predominant decomposition from that of the predominant condensation. Thus it may be assumed that T_{max} is the characteristic value, which accumulates the objective information about the structure and properties of carbon containing materials.

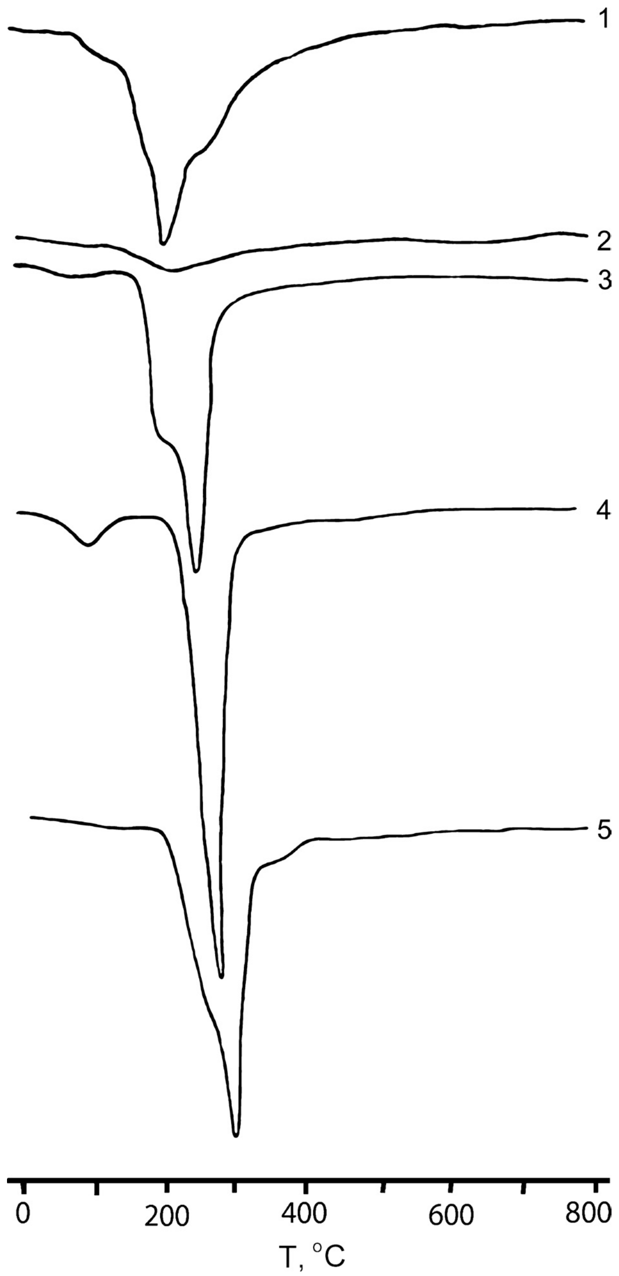
To verify this hypothesis pyrolysis of coal rank at the temperature T_{max} was carried out. The pyrolysis mass balance and regression equations that link the values of the carbon content (C^{daf}) and T_{max} with the technological parameter – pyrolysis tars yield (T^{daf}_{sK}) have been calculated. It has been established that

Samples No (according to the Table 1)	C^{daf} wt%	DTG–data °C		
		T_b	T_{max}	T_e
Coal precursors				
1	44.3	260	320	420
2	51.6	220	330	450
3	52.8	210	310	430
4	56.8	200	275	500
5	57.0	200	300	375
6	59.0	175	295	475
Brown coals				
7	62.4	230	400	485
8	64.1	220	380	550
9	65.4	200	375	500
10	66.8	195	370	540
11	69.6	230	395	490
12	71.0	205	365	550
13	74.3	250	405	500
Low rank bituminous coals				
14	76.6	300	425	500
15	76.2	300	405	480
16	79.0	320	405	480
17	82.2	295	425	500
18	82.7	250	425	510
19	83.5	310	440	530
Middle rank bituminous coals				
20	84.3	370	450	525
21	85.4	365	445	540
22	86.1	370	440	515
23	87.2	340	455	515
24	88.6	395	475	520
25	88.9	360	475	620
High rank bituminous coals				
26	89.7	425	525	660
27	90.3	440	550	650
Anthracites				
28	93.6	520	625	750
29	93.7	525	625	750

■ **Tab. 3.** Temperature region of basic thermal decomposition for coal precursors and different rank coals by using DTG–method.

the pyrolysis tar yield (T^{daf}_{sK}) at the temperature T_{max} decreases regularly for all the carbon containing materials ranging from coal precursors to brown coals and then from hard coals to anthracite. Besides, the relationship between the T_{max}, C^{daf} and T^{daf}_{sK} values (Table 4 and Figs. 3 to 5) can be traced for all the studied samples. It is evident that the coal precursors give high yield of tar during pyrolysis (29.5-16.0 %) within the narrow temperature range of T_{max} – 275-330 °C (Figs. 3 to 5).

Different forms of correlation relationships between experimental parameters have been analyzed [a set of functions $C^{daf} = f(T_{max})$, $T^{daf}_{sK} = f(T_{max})$ and $T^{daf}_{sK} = f(C^{daf})$] with a different type of regression function (linear and squared). Additionally, the relationship between three investigated parameters, i.e. multiple correlations was studied. In this case the analysis has not been confined to the linear function, but also included multiple nonlinear regressions.



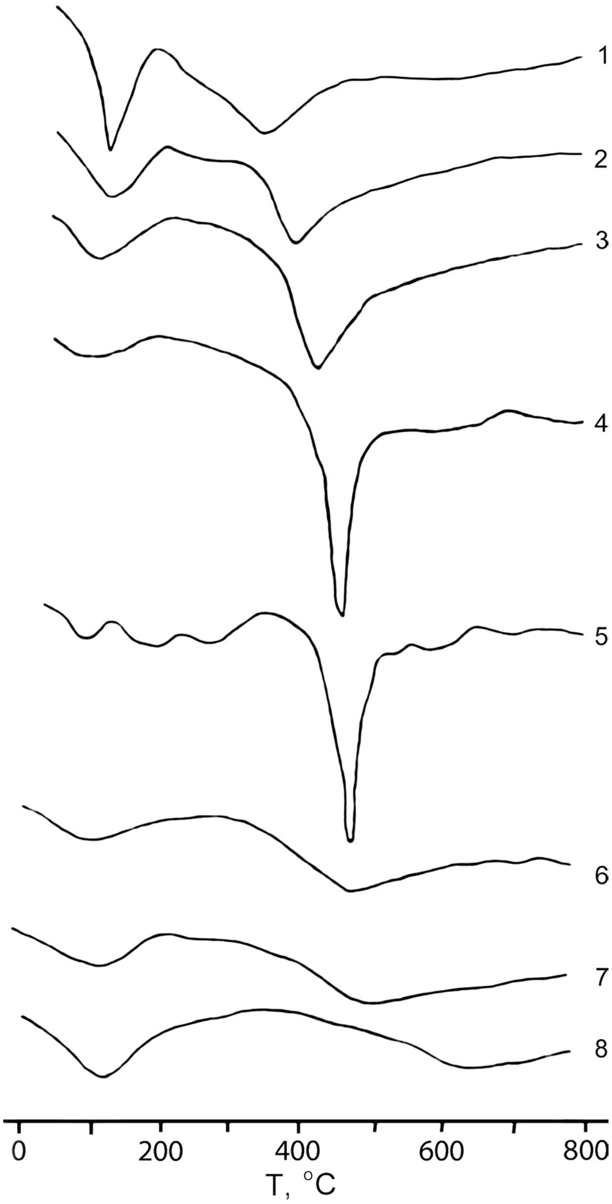
■ **Fig. 1.** DTG curves for coal precursors (C^{daf} %): 1 – lignin (59.0), 2 – peat (57.0), 3 – wood (52.8), 4 – cellulose (44.3), 5 – wood (51.6).

The linear equation for aforementioned functions (equations 1 to 3 [Table 4]) takes the form:

$$y = a_o + a_1x_1 \quad (1)$$

As it is evident from the Table 4 only the dependence between the variables T^{daf}_{sK} and C^{daf} (equation 2) is approximately described within the framework of this approach. The value of the calculated correlation coefficient *r* for all the selected samples is 0.917. The other dependences are not strictly linear because the correlation coefficient (*r*) for them is 0.720–0.820. To obtain a more precise description of these dependences the two–parameters regression equation was used:

$$y = a_o + a_1x_1 + a_2x_2, \quad (2)$$



■ **Fig. 2.** DTG curves for different rank coals (C^{daf} %): 1 – 66.8, 2 – 76.2, 3 – 82.7, 4 – 85.4, 5 – 88.6, 6 – 88.9, 7 – 90.3, 8 – 93.7.

where the variable x_2 is the square of variable x_1.

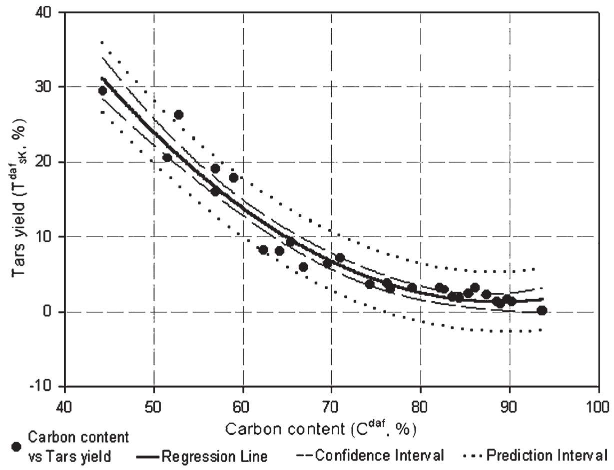
It is known (Batuner et al. 1971, Drejper et al. 1973) that similar functions were successfully used for the description of a wide spectrum of non-linear physical–chemical dependences and permitted to create reliable prognostic models. The use of the parabolic function (equation 4 to 7 in the Table 4) permits to increase the *r* value up to 0.975 (equation 5).

Generally, all the proposed quadratic equations can be used for the prediction of the carbon content and technologic properties of all different coals and coal precursors when only one of the parameters (C^{daf}, T_{max} and T^{daf}_{sK}) is known.

The linear multiple models were obtained by including all three investigated parameters. This resulted in an increase in the correlation coefficient (equation 8 and 9) rather substantial for the function $C^{daf} = f(T_{max}, T^{daf}_{sK})$ ($r = 0.960$).

Equa-tions	Parameters				Coefficient				r	S_o
	Y	x_1	x_2	x_3	a_o	a_1	a_3	A_4		
1	T^{daf}_{sK}	T_{max}			36.5±5.0	–0.07±0.01			0.756	5.4
2	T^{daf}_{sK}	C^{daf}			46.5±3.3	–0.53±0.04			0.917	3.3
3	T_{max}	C^{daf}			10.8±42.9	5.45±0.57			0.880	42.2
4	T^{daf}_{sK}	T_{max}	$(T_{max})^2$		101.3±14.7	–0.37±0.07	0.0003±0.0001		0.873	4.1
5	T^{daf}_{sK}	C^{daf}	$(C^{daf})^2$		119.6±9.9	–2.66±0.28	0.015±0.002		0.975	1.9
6	T_{max}	C^{daf}	$(C^{daf})^2$		705.6±179.9	–14.8±5.2	0.14±0.04		0.927	34.1
7	T_{max}	T^{daf}_{sK}	$(T^{daf}_{sK})^2$		526.9±14.0	–26.1±3.5	0.69±0.13		0.891	41.1
8	C^{daf}	T_{max}	T^{daf}_{sK}		52.6±6.5	0.070±0.013	–1.02±0.14		0.960	4.1
9	T^{daf}_{sK}	T_{max}	C^{daf}		46.3±3.3	0.021±0.015	–0.64±0.09		0.923	3.2
10	T^{daf}_{sK}	T_{max}	C^{daf}	$(T_{max})^2$	72.5±12.3	–0.13±0.07	–0.51±0.10	0.0001±0.0001	0.936	3.0
11	T^{daf}_{sK}	T_{max}	C^{daf}	$(C^{daf})^2$	140.2±10.9	–0.029±0.009	–3.09±0.28	0.0190±0.0022	0.982	1.6
12	T_{max}	C^{daf}	T^{daf}_{sK}	$(C^{daf})^2$	1845.7±400.0	–40.1±9.3	–9.53±3.08	0.284±0.055	0.948	29.5
13	T_{max}	C^{daf}	T^{daf}_{sK}	$(T^{daf}_{sK})^2$	152.1±175.9	4.11±1.92	–12.12±7.33	0.405±0.181	0.909	38.5

■ **Tab. 4.** The results of regression analysis of the investigated dependences for coal precursors and different rank coals.



■ **Fig. 3.** Relation between pyrolysis tars yield (T^{daf}_{sK}) and C^{daf} % content for coal precursors and different rank coals.

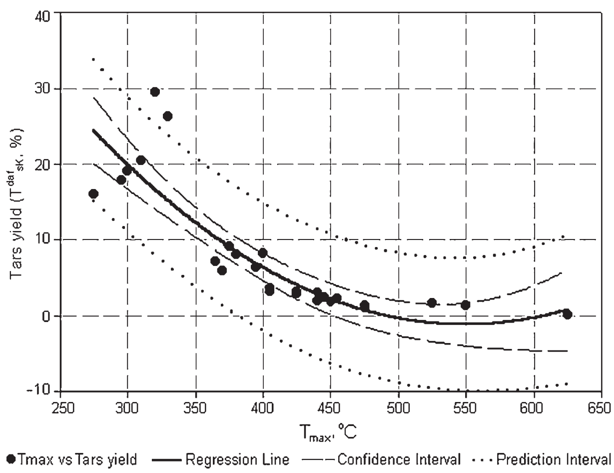
Then the following equations were analyzed:

$$y = a_o + a_1x_1 + a_2x_2 + a_3x_3, \quad (3)$$

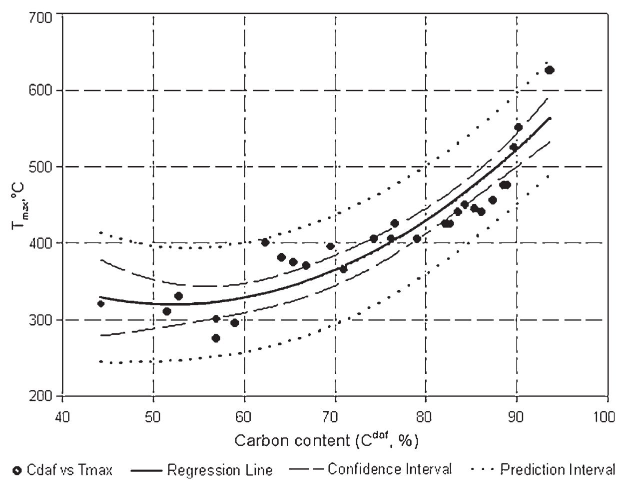
where x_3 is the square of variables x_1 or x_2.

As it is evident from equations 10-13, this leads to a slight improvement in the correlation relationship if $x_3 = (C^{daf})^2$ and aggravation in the case of $x_3 = (T^{daf}_{sK})^2$. The obtained results indicate further complication of the equations by including additional variable parameters is inadvisable, especially from the practical point of view, as it complicates the calculations but fails to considerably improve correlation relationships.

As follows up from all the above, the relationships considered can be divided into two categories with the first one including the function $T^{daf}_{sK} = f(C^{daf})$ for which tightest linear correlation was observed, and the second one involving the functions $T^{daf}_{sK} = f(T_{max})$ and $T_{max} = f(C^{daf})$, which are more exactly described by multiple correlation with quadratic members. The C^{daf} variable influence is more considerable in comparison with T_{max} influence, which is confirmed by the corresponding deviation values of ΔC^{daf} and ΔT_{max} (equation 9) (Table 4). The equations obtained for coal precursors (i.e. samples 1 to 6 in the Table 1) require special consideration. As it is evident from Figs. 3 to 5



■ **Fig. 4.** Relation between pyrolysis tars yield (T^{daf}_{sK}) and T_{max} temperature for coal precursors and different rank coals.

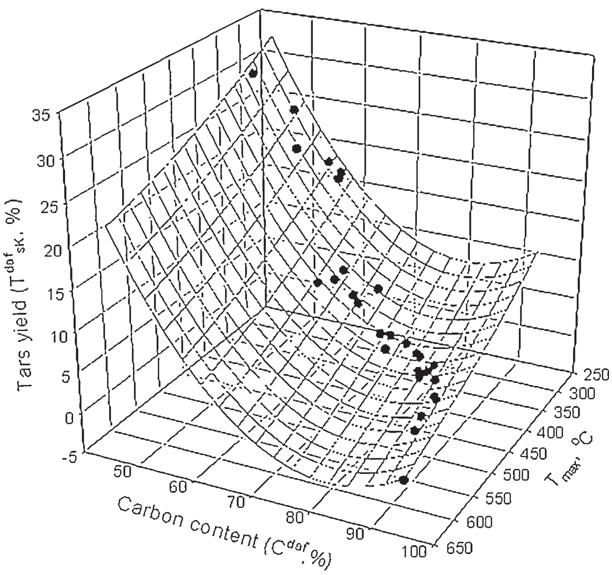


■ **Fig. 5.** Statistic relation found between T_{max} and C^{daf} for coal precursors and different rank coals.

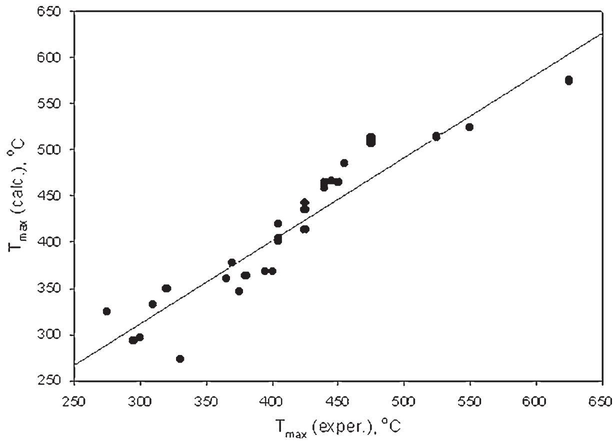
the relations between T_{max}, T^{daf}_{sK} and C^{daf} parameters in this case are close to linear. Unfortunately, the range of variation of these parameters is rather narrow for coal precursors, therefore, appreciable deviation of the calculated data from the experimental ones is be possible during the prediction.

Equations 10 to 13 combining all the three carbon contained materials characteristic considered (C^{daf}, T^{daf}_{sK} and T_{max}) allow us to predict reliably the value of one of them on the basis of the other characteristics. The graphical representation of the function $T_{max} = f(C^{daf}, T^{daf}_{sK})$ shows that the T_{max} parameter can take only definite values which belong to the curve well coinciding with the parabolic surface (Fig. 6). This surface can be correctly described by the following equation including both linear and quadratic parameters:

$$T_{max} = (1{,}800.7 \pm 421.2) - (38.4 \pm 10.4) \cdot C^{daf} - (11.4 \pm 5.7) \cdot T^{daf}_{sK} + (0.27 \pm 0.06) \cdot (C^{daf})^2 + (0.06 \pm 0.16) \cdot (T^{daf}_{sK})^2;$$
$$r = 0.948,\ S_o = 30.04 \qquad (4)$$



■ **Fig. 6.** Parabolic surface with experimental points presented, which describes two parameters equation $T_{max} = f(C^{daf}, T^{daf}_{sK})$ proposed for coal precursors and different rank coals.



■ **Fig. 7.** Comparison of both experimental and calculated temperature T_{max} values for coal precursors and different rank coals.

As it is evident from the Fig. 7 there is good correspondence between the measured and the calculated T_{max} values in this equation.

The collocation of the experimental points for T_{max} on the surface is indicative of legible determination of all the considered T_{max}, C^{daf} and T^{daf}_{sK} values. Absolute and relative errors for the prediction of the T_{max} value were found to be 50 °C and 10–15 %, respectively, i.e. correct enough for the practical aims. Herewith it is possible to disregard the quadrate member $(T^{daf}_{sK})^2$ contribution without sacrifice of the precision of the prediction.

Conclusions

This paper established for the first time that the temperature maximum (T_{max}) of the basic decomposition period obtained by DTA method is an important characteristic of carbon containing materials, which can be used both to evaluate the carbon content (C^{daf}, %) and technological characteristics (T^{daf}_{sK}) of carbon–containing materials and as one of their classification parameters (Shevkoplyas and Galushko 2004).

New mathematical relationships between the composition of various carbon containing materials, the T_{max} values and pyrolysis tar yield (T^{daf}_{sK}) have been found.

Quantitative description of the relationships between C^{daf}, T_{max} and T^{daf}_{sK} experimental values using correlation and regression analysis permitted a sufficiently precise determination of T_{max} values just on the basis of the data of coal elemental analysis (C^{daf}). Proceeding from the experimental data of T_{max}, it is sufficient to estimate the carbon content (C^{daf}) and the pyrolysis tar yield (T^{daf}_{sK}) from carbon containing materials without carrying out the corresponding experiment.

Additionally, the results obtained enable us to improve the method for determination of the yield of pyrolysis products (Standard ISO 647-74 1987) and apply it for all rank coals (C^{daf} = 64.1–93.7 %), including coal precursors (C^{daf} = 44.3–59.0 %) which have not been studied in conjunction with coals up to new. This may initiate a systemic approach in the joint study of coal precursors and different rank coals, could result in more precise formulation of the scientific grounds for combining the latter into a single clasiffication.

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