UDC 62.83

A NEW APPROACH TO EVALUATING THE QUALITY OF COALS

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Abstract

The coals with carbon content C^{daf} = 62,4-93,7 % were studied using thermodecomposition methods. This paper suggests a technique of pyrolysis temperature differentiation taking into account carbon content (C^{daf}, %) and the rank of coal. Simple and multiple regression equations were used to describe quantitative relations between the data V^{daf}, C^{daf}, $(O+N)^{daf}$, temperature T_{max} and pyrolysis tar yield (T^{daf}_{sK}) for different ranks of coals. T_{max} is considered as a parameter which bears information about structure, composition and properties of coals.

Keywords: coal; thermodecomposition; pyrolysis yield; regression equations

Introduction

The search for rational and effective ways of solid fuels processing is the main task that can be solved by thermal methods. It requires determining the optimal conditions and finding new express-methods which would help to estimate thermal transformations. Today there are some well-known methods for testing coal properties and their behavior in different thermal processes. Among them are genetic, industrial and industrial-genetic classifications covering coal ranks from brown coals to anthracite ones. However, these methods are based on the early-established stereotypes in understanding of the coal structure. One of such methods is the widely applied “method of defining semi-coking products yield” (Standard ISO 647-74, 1987). The main disadvantage of this method is the fixed temperature of pyrolysis - 520 ^{o}C, which does not correspond to TGA data and cannot be spread on all ranks of coal. Previously the authors developed a method of coal-bearing materials thermodestruction at minimal temperature which can be helpful in studying the structures of various carbon-base materials [2].

Recently a number of works have been published which describe the use of mathematical-statistical analysis to estimate the relation between the petrographic composition of coals and their basic physical-chemical and technologic properties [4, 5, 6]. Thus the application of mathematical-statistical analysis can help to develop new effective methods for investigating the structure and technological characteristics of coal-based materials. In this paper the interconnection of experimental values C^{daf}, T_{max} and T^{daf}_{sK} has been described by means of correlation and regression analysis.The aim of the paper is to study the prospects of using thermodecomposition methods to reveal new quantitative characteristics which would reflect the composition and structure of coals of different ranks. This paper is also aimed at describing the quantitative relations between technical and elemental coal composition (V^{daf}, C^{daf}, $(O+N)^{daf}$), pyrolysis temperature T_{max} and tar yield (T^{daf}_{sK}) for all ranks of coals.

Materials and Methods

The research was carried out on brown coals, hard coals and anthracites, which contain (%): C^{daf}=62.41–93.7; H^{daf} = 6,1 - 1,9; V^{daf} = 63,2 - 4,2; $O+N^{daf}$ = 28,5 - 2,4. Chemical nature of coals can be investigated by studying the products of pyrolysis. In this case only the primary products of coal decomposition should be analyzed. However, these products can enter the reactions of condensation, polymerization, isomerization, etc. Thus they are transformed into secondary products, and their properties and composition depend upon the conditions of the process. Differential thermal analysis (TGA–method) of the samples allows defining this temperature.

This method helps to trace the changes in the mass (DTG and TG-curves) and the thermal effects (DTA). So it is possible to obtain valuable information about the behavior of coals heated up to 950 ^{o}C and to study the process at each particular temperature. To our mind the most important TGA data are the temperature range and maximum temperature (T_{max}) of the endoeffect. The method allows differentiating the temperature of coal treatment to define T_{max} for each particular sample taking into account the content of carbon (C^{daf}). Differential thermal analysis was carried out in a Paulik–Paulik–Erdey Q-1500D in a closed platinum crucible; 500 mg of coal were heated with the rate 10^oC /min^{-1}. The analysis of TG-DTG curves was performed in order to estimate T_{max}, T_b (beginning) and T_e (end) of the basic coal thermodecomposition region defined by TGA–method [3].

Sample coals pyrolysis was carried out in a fixed bed reactor (volume 20 cm^3). The sample (2-10 g, fraction ≤ 0.5 mm) was heated at the rate of 25^o C /min^{-1} up to the temperature T_{max} and held at this temperature for 10 min. At the end of experiment the pyrolysis water, tar, gas and solid residue yields were estimated by the weight of the products; then the mass balance of the process was calculated.

Discussion and Conclusion

On the basis of DTG–curves, the values of T_b, T_{max} and T_e were calculated for the basic decomposition region (Table 1). As it is seen from Table 1, the higher is the rank of the coal the higher are T_b, T_{max} and T_e values. The evolution of these parameters during coalification testifies to the fact that they are much influenced by coal nature. Therefore the above mentioned temperature range is specific for each coal sample and reflects both general peculiarities of coal structure and particular features at a particular metamorphism stage. The temperature maximum T_{max} corresponds to the highest rate of the mass loss. It is a temperature point, which separates the temperature range where destruction prevails from the range where the rate of condensation processes is higher then the rate of destruction. Thus, we can state that T_{max} is the characteristic value that bears objective information about the coal structure.

Table 1. Temperature region of the basic thermodecomposition for different rank coals using DTA–method.

Coals Number	C^{daf}, %	DTG–data, °C		
		T_b	T_{max}	T_e
1.	62.4	230	400	485
2.	64.1	240	380	475
3.	65.4	200	375	470
4.	66.8	195	370	445
5.	69.6	230	395	490
6.	71.0	205	365	450
7.	74.3	250	405	450
8.	76.6	300	425	450
9.	76.2	325	405	440
10.	79.0	320	405	430
11.	82.2	290	425	450
12.	82.7	250	425	510
13.	83.5	360	440	530
14.	84.3	370	450	525
15.	86.1	350	440	515
16.	85.4	350	445	500
17.	87.2	340	455	515
18.	88.6	395	475	490
19.	88.9	390	470	525
20.	89.7	425	525	660
21.	90.3	430	550	650
22.	93.6	520	620	650
23.	93.7	525	625	745

To verify this hypothesis the pyrolysis of different coal samples was carried out at the temperature T_{max}. We calculated the mass balance of the pyrolysis process and obtained the regression equations that connect the values of C^{daf} and T_{max} with pyrolysis tar yield (T^{daf}_{sK}). If pyrolysis is carried out at the temperature T_{max} the tar yield decreases. In this case we can observe the interconnection between T_{max}, C^{daf} and T^{daf}_{sK} (Table 2 and Figure 1-3) for all samples under investigation. We analyzed different types of correlations between C^{daf}, T_{max} and T^{daf}_{sK} values by the methods of regression and correlation analysis. Correlation coefficient (r) and standard deviation of dependent variables (S_o) were used to estimate the relation between the above mentioned parameters. The significance of regression equation coefficients was estimated by Student criterion and the adequacy of these equations was estimated by Fisher criterion, the rate of significance being 95% [7].

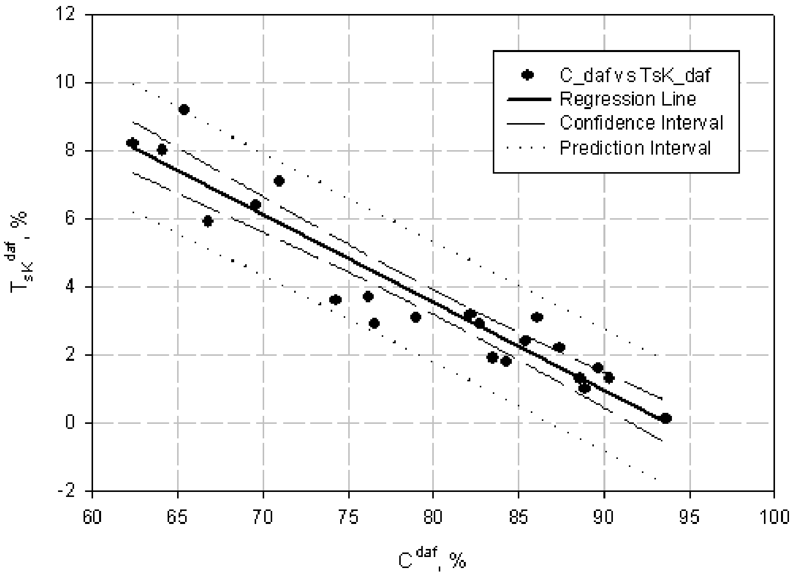

Figure 1. Relation between pyrolysis tar yield T^{daf}_{sK} and C^{daf} content for different ranks of coals

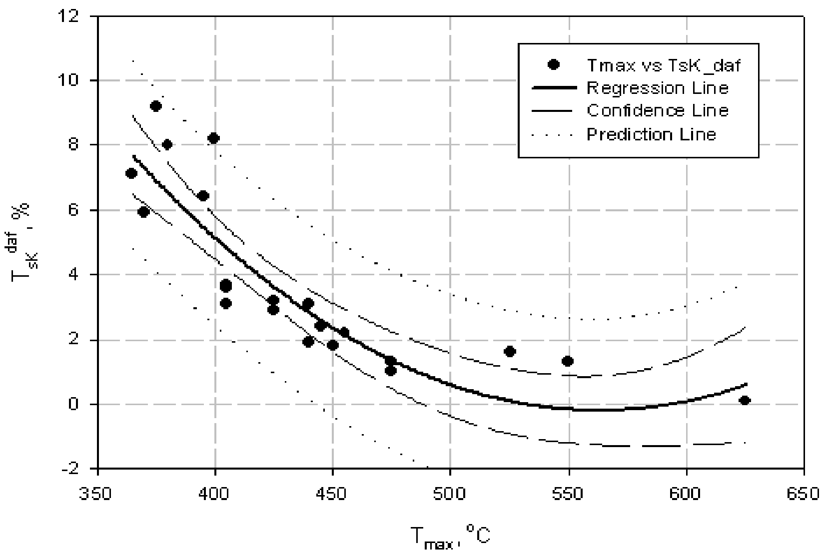

Figure 2. Relation between pyrolysis tar yield T^{daf}_{sK} and T_{max} temperature for different ranks of coal

Table 2. Results of regression analysis describing the quantitative relations between C^{daf} content, T_{max} temperature and pyrolysis tar yield (T^{daf}_{sK}) for different ranks of coal

Equations	Parameters				Coefficients				r	S_o
	y	x_1	x_2	x_3	a_o	a_1	a_2	a_3		
1	T^{daf}_{sK}	T_{max}	-	-	16.0±2.3	−0.028±0.005	-	-	0.767	1.74
2	T^{daf}_{sK}	C^{daf}	-	-	24.2±1.5	−0.26±0.02	-	-	0.950	0.85
3	T_{max}	C^{daf}	-	-	−44.1±74.3	6.13±0.92	-	-	0.824	42.1
4	T^{daf}_{sK}	T_{max}	$(T_{max})^2$	-	63.9±11.3	−0.23±0.05	0.00021±0.00004	-	0.886	1.29
5	T^{daf}_{sK}	C^{daf}	$(C^{daf\,2}$	-	47.5±12.8	−0.86±0.33	0.0039±0.0021	-	0.957	0.80
6	T_{max}	C^{daf}	$(C^{daf\,2}$	-	2545.9±366.9	−61.21±9.50	0.43±0.06	-	0.953	23.0
7	T_{max}	T^{daf}_{sK}	$(T^{daf}_{sK})^2$	-	599.6±15.4	−76.2±8.7	6.05±0.92	-	0.932	27.5
8	T^{daf}_{sK}	T_{max}	C^{daf}	-	24.3±1.5	0.002±0.004	−0.27±0.03	-	0.950	0.86
9	T_{max}	C^{daf}	T^{daf}_{sK}	-	−144.6±278.4	7.20±3.01	4.15±11.08	-	0.825	43.0
10	T^{daf}_{sK}	T_{max}	C^{daf}	$(T_{max})^2$	30.6±10.3	−0.031±0.052	−0.25±0.05	0.00008±0.00002	0.951	0.88
11	T^{daf}_{sK}	T_{max}	C^{daf}	$(C^{daf})^2$	90.1±21.3	−0.017±0.007	−1.89±0.52	0.0111±0.0036	0.967	0.72
12	T_{max}	C^{daf}	T^{daf}_{sK}	$(C^{daf})^2$	3196.9±428.9	−73.1±9.9	−13.71±5.76	0.48±0.06	0.964	20.7
13	T_{max}	C^{daf}	T^{daf}_{sK}	$(T^{daf}_{sK})^2$	448.5±211.4	1.58±2.21	−67.3±15.1	5.69±1.06	0.934	27.8

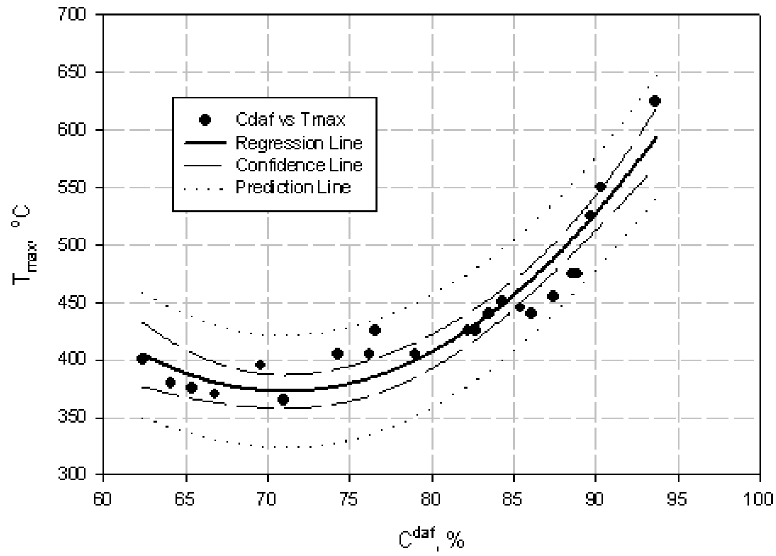

Figure 3. Relation between Tmax temperature and Cdaf for different ranks of coal

Different forms of correlations between experimental parameters were analyzed [a set of functions $C^{daf} = f(T_{max})$, $T^{daf}_{sK} = f(T_{max})$ and $T^{daf}_{sK} = f(C^{daf})$]. The analysis was not confined to linear connections only. We involved multiple regressions using mathematical expressions of a straight/curve line for each independent variable.

The linear regression equations for aforementioned functions are presented in Table 2:

$$y = a_o + a_1 x_1 \qquad (1)$$

Table 2 shows that the dependence between T^{daf}_{sK} and C^{daf} (equation 2) is the only relation which can be properly described within this approach. Correlation coefficient r for all selected samples was 0.950. Other dependences were not strictly linear because the correlation coefficient was 0.767–0.824. For a more precise description we used the expression of two-parameter regression where x_2 is square x_1:

$$y = a_o + a_1 x_1 + a_2 x_2, \qquad (2)$$

It is a well known fact [8, 9] that similar functions can be used to describe a great variety of non-linear physical–chemical dependences. So reliable prediction models can be developed. In general all the above mentioned quadratic dependences can be used in predicting the composition and properties of the coal of all ranks if one of the parameters (C^{daf}, T_{max} and T^{daf}_{sK}) is known. We obtained a linear multiple prediction model, which includes all the three parameters. It increased the correlation coefficient for $T^{daf}_{sK} = f(T_{max})$ (equations 1, 4) and didn't influence the function $T^{daf}_{sK} = f(C^{daf})$ (equations 1,2 and 7). Thus, for equations 1, 2 and 7 correlation coefficient r is 0.767, 0.950 and 0.950 respectively. Then the following equations were analyzed:

$$y = a_o + a_1 x_1 + a_2 x_2 + a_3 x_3, \qquad (3)$$

where x_3 is the square of variables x_1 or x_2.

As it is seen from equations 8-11 such a regression slightly improves the correlation if $x_3 = (C^{daf})^2$ and worsens it if $x_3 = (T^{daf}_{sK})^2$. The obtained results showed that further complication (involving additional variables) is not reasonable as it makes calculations more difficult and does not improve correlations. Proceeding from the above mentioned facts we can divide the dependences into two categories. The first one is $T^{daf}_{sK} = f(C^{daf})$. It is characterized by the closest correlation and is described with a linear regression function. The functions $T^{daf}_{sK} = f(T_{max})$ and $T_{max} =$

$f(C^{daf})$ can be referred to the second category. They are more precisely described by multiple regression equations with quadratic terms included. The influence of the independent factor C^{daf} is maximal and exceeds the influence of T_{max}. It is explained and confirmed by the value of standard deviation, S_o (Table 2).

For quantitative description of the dependences between parameters T_{max}, V^{daf} and $(O+N)^{daf}$ we used the equations of linear regressions $V^{daf} = f(T_{max})$, $V^{daf} = f(C^{daf})$, $T_{max} = f((O+N)^{daf})$ presented in Table 3. Figure 4 shows that T_{max}–V^{daf} relation (equations 3, 6, Table 3) can be described well using this approach; and correlation coefficient *r* is 0,923-0,985 for all samples.

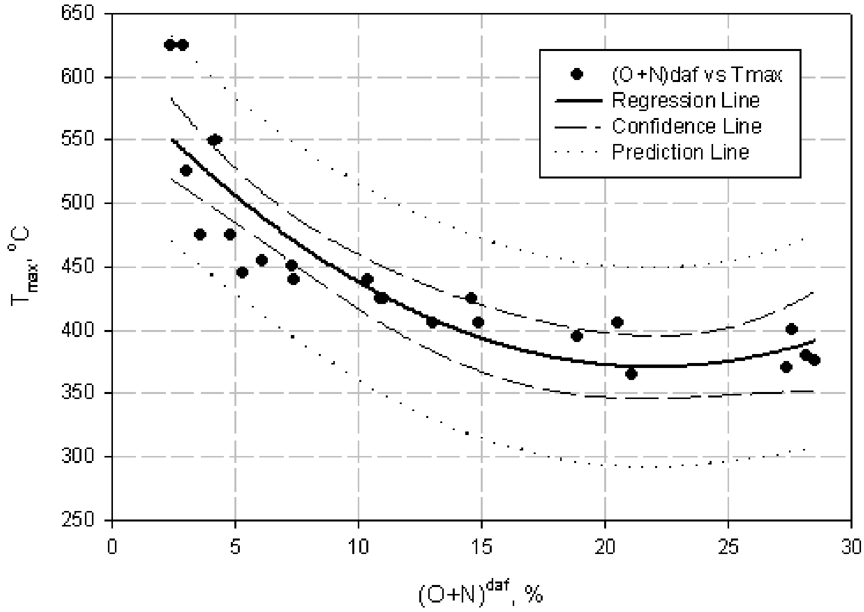

Figure 4. Relation between T_{max} temperature and $(O+N)^{daf}$ for different ranks of coal

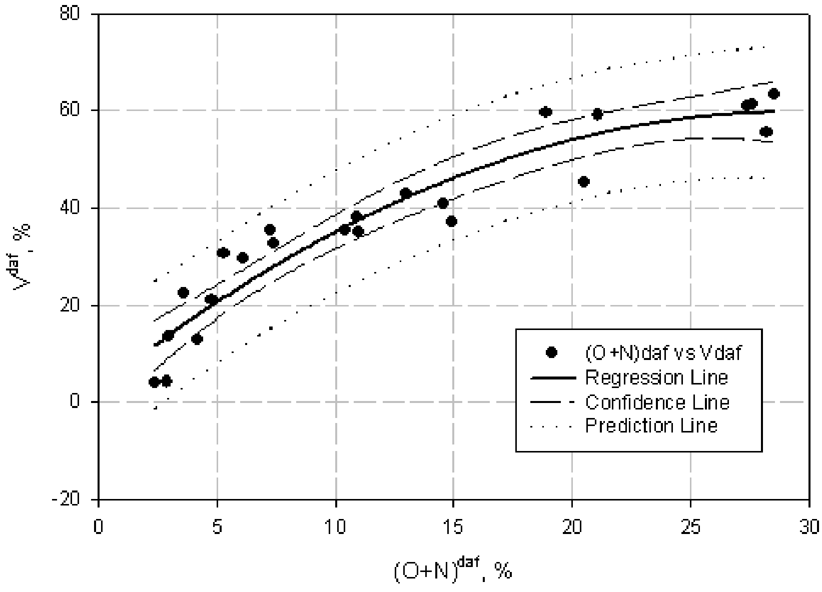

Figure 5. Relation between volatile yield V^{daf} and $(O+N)^{daf}$ for different ranks of coal

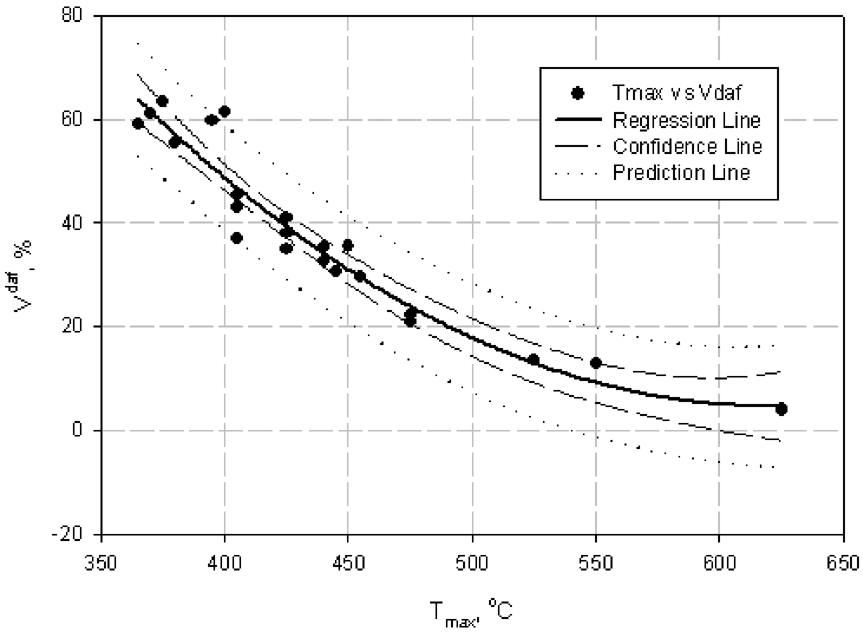

Figure 6. Relation between T_{max} temperature and volatile yield V^{daf} for different ranks of coal

Other dependences (Figures 5-6) are non-linear and require more complex equations (equations 1, 2, 4, 5, Table 3) .Correlation coefficients will grow significantly if we use two-parameter regression equations, where the variable x_2 is the square of the variable x_1 (equations 4-6, Table 3).

The use of equations 7-9 increases correlation coefficients up to 0,942-0,979. Therefore, all considered dependences can be used to predict the structure and properties of coals if we know one or two of the experimental parameters: $(O+N)^{daf}$, T_{max} or V^{daf}.

The analysis of dependences: T_{max} $(O+N)^{daf}$ or V^{daf} (equations 7-9, Table 3) shows that it is possible to predict one of the parameters proceeding both from the table data and from the experimental values of the other parameters. It is evident that three-parameter regression equations with quadratic terms (equations 10-13, Table 3) do not improve the correlation. Regression equations (Table 3) are used to precisely define the values of the temperature T_{max} on the basis of technical and elemental analysis data (V^{daf}, $(O+N)^{daf}$). They also allow estimating the content of oxygen (O^{daf}) and nitrogen (N^{daf}) and/or the volatile yield (V^{daf}) from different coals using TGA–data.

Therefore it is possible to make a conclusion that the maximum thermodecomposition temperature T_{max} is a very important parameter for coals of all ranks. It can be used in estimating the composition and properties of coals. It is also applied as a parameter of coals classification [2]. This paper suggests mathematical dependences which describe quantitative relations between (V^{daf}, C^{daf}, $(O+N)^{daf}$), pyrolysis temperature T_{max} and tar yield (T^{daf}_{sK}) for all coal ranks. The obtained results were used to improve the method of estimating the yield of pyrolysis products heating them at the maximum decomposition temperature T_{max}.

Table 3. Results of regression analysis describing the quantitative relations between $(O+N)^{daf}$ content, T_{max} temperature and volatile yield (V^{daf}) for different ranks of coal

Equa-tions	Parameters				Coefficients				r	S_o
	y	x_1	x_2	x_3	a_o	a_1	a_2	a_3		
1	$(O+N)^{daf}$	T_{max}	-	-	55.6±7.8	−0.09±0.02	-	-	0.772	5.8
2	$(O+N)^{daf}$	V^{daf}	-	-	−3.97±1.72	0.46±0.04	-	-	0.920	3.6
3	T_{max}	V^{daf}	-	-	582.2±13.6	−3.70±0.34	-	-	0.923	28.5
4	$(O+N)^{daf}$	T_{max}	T_{max}^2	-	242.3±32.0	−0.87±0.13	0.0008±0.0001	-	0.923	3.6
5	$(O+N)^{daf}$	V^{daf}	$(V^{daf})^2$	-	1.97±2.17	0.003±0.132	0.0065±0.0018	-	0.952	2.9
6	T_{max}	V^{daf}	$(V^{daf})^2$	-	649.8±9.9	−8.87±0.60	0.074±0.008	-	0.985	13.1
7	$(O+N)^{daf}$	T_{max}	V^{daf}	-	−42.1±14.1	0.06±0.02	0.70±0.09	-	0.942	3.2
8	V^{daf}	T_{max}	$(O+N)^{daf}$	-	82.0±9.4	−0.13±0.02	1.03±0.14	-	0.979	3.8
9	T_{max}	V^{daf}	$(O+N)^{daf}$	-	598.5±13.4	−5.58±0.75	4.10±1.51	-	0.944	25.0
10	$(O+N)^{daf}$	T_{max}	V^{daf}	T_{max}^2	74.3±53.6	−0.34±0.18	0.48±0.13	0.0004±0.0002	0.955	2.9
11	$(O+N)^{daf}$	T_{max}	V^{daf}	$(V^{daf})^2$	17.3±32.6	−0.02±0.05	−0.21±0.46	0.008±0.004	0.953	2.9
12	T_{max}	V^{daf}	$(O+N)^{daf}$	$(V^{daf})^2$	650.7±10.3	−8.87±0.61	−0.49±1.04	0.077±0.011	0.985	13.4
13	T_{max}	V^{daf}	$(O+N)^{daf}$	$((O+N)^{daf})^2$	611.7±15.3	−4.72±0.91	−2.41±4.36	0.16±0.10	0.951	24.1

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Received on 02.03.2010