Acta Geodyn. Geomater., Vol.3, No.2 (142), 51-55, 2006

THE EVALUATION OF CHARS REACTIVITY USING THERMOGRAVIMETRY AND MULTIVARIATE STATISTICAL METHOD

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(*Received* January 2006, *accepted* May 2006)

ABSTRACT

The reactivity of a char depends very on the parent coal. Much information about correlation between properties of coal and reactivity of chars is lost by using only standard methods for a large dataset evaluation. In this research a set of 8 coals has been investigated by thermal analysis and reactivity of obtained chars was analyzed as a function of properties of parent coal properties using Canonical correlation analysis. The reactivity of chars was determined by thermogravimetric analysis of non-isothermal combustion in oxygen. It can be stated that methods of multivariate data analysis are useful tools for the interpretation of coal chars reactivity data.

KEYWORDS: coal, chars, thermal analysis, canonical correlation analysis, reactivity

1. INTRODUCTION

The application of thermal analysis techniques to study pyrolysis of coal (Chermin and van Krevelen, 1957; Mianowski and Radko, 1995; Das, 2001;) and reactivity of chars (Beamish et al., 1998; Shaw et al., 1997; Stenseng et al., 2001) gained a wide acceptance. Our understanding of the char combustion process has improved, identification and interpretation of relationships between char reactivity and parent coal properties remains a challenging topic. It is established that petrographic composition, reflectance, chemical properties and ash chemistry of coals all influence the reactivity of chars (Folgueras et al., 2003; Hurt and Gibbins, 1995; Hurt and Calo, 2001; Jenkins et al., 1973; Jüntgen, 1984; Lang and Hurt, 2002; Méndez et al., 2003; Mianowski and Radko, 1995; Miura et al., 1989; Radko and Mianowski 1998; Radovic and Walker, 1984; Radovic et al., 1991; Sun et al., 2003; Tomita et al., 1977). The purpose of this paper was to present potential application of canonical correlation analysis to evaluate correlation of many coal parameters with reactivity of chars.

2. EXPERIMENTAL

2.1. *SAMPLE PREPARATION*

Samples of eight coals of different rank were obtained from Upper Silesian Basin and Lower Silesian Basin (Poland). From every single coal three samples were obtained by sink-float separation in heavy liquids: light fraction (density <1.30 g cm^{-3}), medium fraction (density 1.30-1.35 g cm^{-3}), heavy fraction (density > 1.35 g cm^{-3}). A method of density separation was performed to obtain coal samples covering a wide range of maceral and mineral matter content. The light fractions contain higher amount of liptinite in comparison to parent coals with almost absence of mineral matter. The medium fractions have similar petrographic composition to parent coals with significant lower content of mineral matter. The heavy fractions contain higher content of inertinite and mineral matter in comparison to parent coals.

Standard methods have been used in sample preparation and chemical tests. The ultimate, proximate and petrographic data for all samples are presented in Table 1. Major elements in ash were determined using atomic absorption spectrometry (AAS) instead of standard procedures (Maes et al., 1997). Reflectance and petrographic composition analyses were carried out using a reflected light Zeiss microscope (500 points) on epoxy impregnated polished coal grain mounts.

2.2. *PYROLYSIS OF COALS*

Modeling coal pyrolysis using kinetic methods demonstrate that thermal decomposition of coal proceeds in two stages. It is shown that that pyrolysis in the temperature range 280-580°C is a first-order process with non-linear weight losses vs. temperature dependence (the kinetic regime). In the second stage the same relationship acquire the linear form (the diffusion regime) Then pyrolysis could be described in two different activation energies, $E>0$ and $E \rightarrow 0$.

Table 1 Properties of coals, kinetic parameters of pyrolysis and reactivity of chars

Sample identification	Properties of coals																	Kinetic parameters of pyrolysis							Reactivity of chars	
	Set 1						Set 2				Set 3							Set 4							Set 5	
	W	A	VM	RI	C	H	V	L	I	M	Si	Al	Ca	Fe	Mg	K	Na	$T_{K.i}$	$T_{K.f}$	$T_{D.i}$	$T_{D.f}$	E_a	A_K	A_D	k	PIO
A (R_0=0.76*)	3.7	3.5	32.8	33	84.6	4.73	45	11	44	0	0.28	0.21	0.69	0.34	0.21	0.02	0.06	593	770	665	1111	135	150 x10^4	0.062	1.06	677
A-L	3.1	0.7	36.0	38	83.2	4.83	55	20	25	0	0.06	0.04	0.14	0.07	0.04	0.00	0.01	613	752	659	1014	173	340 x10^4	0.108	0.62	703
A-M	3.2	2.1	32.6	18	83.2	4.04	42	13	45	0	0.17	0.13	0.41	0.20	0.13	0.01	0.04	610	744	681	987	164	490 x10^4	0.141	0.63	696
A-H	3.4	5.4	30.7	17	86.8	4.96	28	9	62	1	0.43	0.32	1.06	0.52	0.33	0.02	0.10	633	758	675	1016	171	320 x10^4	0.067	0.82	696
B (0.89)	1.2	2.3	30.6	43	85.9	5.01	58	13	28	1	0.11	0.11	0.18	0.83	0.06	0.01	0.03	558	835	674	1100	86	4.3 x10^4	0.062	0.76	682
B-L	0.9	0.5	32.4	68	85.6	5.27	63	15	21	1	0.02	0.02	0.04	0.18	0.01	0.00	0.01	624	773	688	1022	161	260 x10^4	0.087	0.44	696
B-M	3.1	1.5	27.7	17	86.0	4.89	49	7	39	5	0.07	0.07	0.12	0.54	0.04	0.00	0.02	647	779	671	1082	158	230 x10^4	0.065	0.44	698
B-H	1.4	8.8	21.7	15	85.5	4.43	30	3	58	9	0.43	0.44	0.68	3.19	0.24	0.02	0.11	577	822	681	1031	90	12 x10^4	0.056	0.68	666
C (0.90)	1.9	6.4	32.7	32	82.3	5.35	74	8	17	1	1.83	0.92	0.30	0.38	0.15	0.09	0.06	572	792	669	1069	107	55x10^4	0.072	0.60	680
C-L	0.5	2.2	34.4	50	82.1	5.51	77	14	9	0	0.63	0.32	0.10	0.13	0.05	0.03	0.02	621	787	688	1077	147	190 x10^4	0.077	0.55	709
C-M	0.8	4.5	33.4	23	82.2	5.29	74	8	18	0	1.28	0.65	0.21	0.27	0.11	0.06	0.04	601	792	696	1070	119	86 x10^4	0.072	0.55	688
C-H	1.0	16.0	32.6	20	85.5	5.47	60	6	31	3	4.57	2.29	0.76	0.96	0.38	0.23	0.15	610	789	684	1062	127	110 x10^4	0.062	0.48	721
D (1.06)	0.4	6.6	26.3	88	88.3	5.36	67	8	21	4	1.50	0.83	0.60	0.48	0.08	0.10	0.06	603	808	683	1063	119	85 x10^4	0.066	0.52	701
D-L	0.3	1.7	26.8	86	87.6	5.28	76	10	12	2	0.39	0.21	0.15	0.12	0.02	0.03	0.02	640	778	700	1040	152	150 x10^4	0.080	0.44	729
D-M	0.3	4.8	26.2	78	87.4	5.26	68	7	22	3	1.09	0.61	0.44	0.35	0.05	0.07	0.04	658	767	701	1029	210	530 x10^4	0.077	0.54	668
D-H	0.3	29.5	25.9	60	88.0	4.98	37	3	38	22	6.71	3.73	2.69	2.12	0.34	0.46	0.26	670	760	700	1020	140	140 x10^4	0.075	0.55	688
E (1.09)	1.1	6.1	26.0	48	87.3	5.02	54	8	37	1	1.55	0.83	0.28	0.44	0.13	0.08	0.05	579	820	684	1011	101	35 x10^4	0.080	0.52	693
E-L	1.1	1.8	27.3	63	86.8	5.15	67	11	22	0	0.46	0.25	0.08	0.13	0.04	0.02	0.01	578	837	689	1072	96	22 x10^4	0.079	0.43	687
E-M	1.1	3.8	25.3	23	87.3	4.91	57	6	36	1	0.96	0.52	0.18	0.27	0.08	0.05	0.03	603	793	694	1024	99	25 x10^4	0.077	0.42	700
E-H	0.6	17.0	25.4	19	88.6	4.76	29	2	67	2	4.31	2.32	0.79	1.22	0.36	0.24	0.13	593	832	690	1022	97	24 x10^4	0.078	0.49	679
F (1.10)	0.6	6.5	22.4	72	88.2	4.87	61	6	28	5	1.75	0.98	0.15	0.60	0.06	0.12	0.07	593	843	700	1013	93	13 x10^4	0.084	0.59	693
F-L	1.1	3.9	24.6	80	89.5	5.14	73	7	18	2	1.05	0.59	0.09	0.36	0.03	0.07	0.04	647	800	705	1045	171	280 x10^4	0.079	0.43	744
F-M	1.0	4.9	21.1	50	87.9	4.84	48	6	43	3	1.32	0.74	0.12	0.45	0.04	0.09	0.05	660	823	723	998	156	200 x10^4	0.098	0.36	699
F-H	1.0	11.9	20.8	25	88.6	4.80	42	6	46	6	3.20	1.80	0.28	1.10	0.11	0.22	0.13	644	798	700	1080	143	160 x10^4	0.058	0.41	683
G (1.20)	0.4	6.5	22.8	65	87.6	5.10	57	7	33	3	1.37	1.03	0.38	0.69	0.07	0.10	0.06	581	849	695	1018	92	11 x10^4	0.078	0.36	684
G-L	0.3	2.9	24.5	70	87.4	4.91	74	8	16	2	0.61	0.46	0.17	0.31	0.03	0.04	0.03	591	831	696	964	103	37 x10^4	0.097	0.49	720
G-M	0.6	10.0	23.4	30	86.5	4.67	48	11	38	3	2.11	1.59	0.59	1.06	0.10	0.15	0.10	674	815	705	993	161	230 x10^4	0.079	0.42	710
G-H	1.0	12.3	22.7	22	89.1	4.64	37	7	48	5	2.60	1.96	0.72	1.31	0.13	0.19	0.12	633	806	697	1015	139	150 x10^4	0.067	0.41	703
H (3.18)	2.5	12.3	7.6	0	91.0	2.67	83	0	11	6	3.18	1.96	0.31	1.20	0.09	0.20	0.23	693	924	777	1003	97	1.9 x10^4	0.079	0.52	698
H-L	1.3	2.1	5.9	0	92.1	2.83	96	0	4	0	0.54	0.33	0.05	0.21	0.02	0.03	0.04	688	929	791	1055	111	26 x10^4	0.066	0.49	691
H-M	1.9	3.7	5.6	0	93.0	2.89	98	0	2	0	0.96	0.59	0.09	0.36	0.03	0.06	0.07	712	909	821	1053	122	52 x10^4	0.076	0.61	693
H-H	1.0	22.9	7.7	0	94.3	2.96	71	0	10	19	5.92	3.65	0.58	2.24	0.17	0.38	0.43	723	989	786	1019	104	0.36 x10^4	0.078	0.49	699

$^*R_0$- mean random vitrinite reflectance (%), W- moisture (%), A- ash (%, dry), VM- volatile matter (%, dry and ash free), RI- Roga Index (%), C- carbon (%, dry and ash free), H- hydrogen (%, dry and ash free), V-vitrinite (%vol), L-lipinite (%vol), I- inertinite (%vol), M-mineral matter (%vol), Si, Al, Ca, Fe, Mg, K, Na- amount of element in coal (%, dry), $T_{K,i}$- initial temperature of kinetic regime (°C), $T_{K,f}$- final temperature of kinetic regime (°C), $T_{D,i}$- initial temperature of diffusion regime (°C), $T_{D,f}$- final temperature of diffusion regime (°C), A_K ,A_D- pre-exponential factors of the Arrhenius equation for kinetic and diffusion regimes, respectively (min^{-1}), E_a-activation energy (kJ mol^{-1}), k- kinetic constant of combustion (mg min^{-1}), PIO- point of initial oxidation (K)

Two equation types describe the pyrolysis process:

- the first order kinetics:

$$-\ln(1-\alpha_K)=\frac{A_K R T^2}{qE}\exp\left(-\frac{E}{RT}\right),\quad \alpha_K\in\langle 0.1\rangle \tag{1}$$

where: $\alpha_k=\dfrac{m_{k,i}-m(T)}{m_{k,i}-m_{k,f}}$

- for the kinetics of the first order if assumed that according to $E\rightarrow 0$ in Eq. (1):

$$-\ln(1-\alpha_D)=\frac{A_D}{q}\Delta T,\quad \Delta T=T-T_{D,i}\quad \text{i}\quad \alpha_D\in\langle 0.1\rangle \tag{2}$$

where: $\alpha_D=\dfrac{m_{D,i}-m(T)}{m_{D,i}-m_{D,f}}$

where A is a pre-exponential factor of the Arrhenius equation, min^{-1}; E is an activation energy, kJ mol^{-1}; m is a mass of the sample, mg; q is a rate of heating, deg min^{-1}; R is universal gas constant, R = 0.008314 kJ(mol K)^{-1}; T is absolute temperature, K; α is a degree of conversion (subscript: i – initial stage, final stage, K – refers to kinetic regime, D – refers to diffusion regime).

The eight raw coals and the twenty-four fractions were subjected to non-isothermal thermogravimetric analysis (TGA). The TGA analysis was performed at a heating rate of 10 K min^{-1} (inert atmosphere, argon). The kinetic parameters of pyrolysis for every sample were estimated and presented in Table 1.

2.3. *REACTIVITY OF CHARS OBTAINED DURING PYROLYSIS*

Several parameters can be used to express char reactivity. One of them can be point of initial oxidation (PIO) (Suzin et al., 1999). The PIO is defined as the temperature at which the TG reading is 0.1% smaller than the running average of the five prior data points. As a second parameter we used kinetic constant of combustion k. For the TG curves obtained during combustion of chars in the range of the best fit of experimental data to a linear relationship describing the mass loss as a function of temperature (Minkina and Mianowski, 2000). The chars obtained during pyrolysis of coal samples were subjected to the TGA analysis in oxygen stream 15 dm^3 h^{-1}, at a heating rate of 10 K min^{-1}. For every sample 10 mg of chars were spread out carefully on the sample holder composed of platinum plate. The parameters of reactivity for every char were estimated and presented in Table 1.

2.4. *CANONICAL CORRELATION AND REDUNDANCY ANALYSIS*

Canonical correlation analysis (CCA) operates on two sets of variables, x_i, i=1,2,…,p, and y_j, j=1,2,,…,q. CCA finds a linear combination from each set, called a canonical variable, such that the canonical correlation (R_c) between the two canonical variables is maximized. The coefficients of the linear combinations are canonical coefficients or canonical weights. CCA continues by finding a second set of canonical variables, uncorrelated with the first pair that produces the second highest correlation coefficient. The process of constructing canonical variables continues until the number of pairs of canonical variables equals the number of variables in the smaller group. The canonical correlations can be squared to compute the proportion of variance shared by the sum scores (canonical variables) in each set. If this proportion is multiplied by the proportion of variance extracted, you arrive at a measure of *redundancy*. The criterion of redundancy was meant as another tool to help the investigator assess the usefulness of particular canonical variables. Redundancy can be interpreted as the fraction of variance in one set that can be explained by the other. This technique of multivariate analysis is a useful tool for summarizing the information contained in large set of data. However, canonical variables may not necessarily account for much of the variation in the data, CCA gives a possibility to get an overall picture of the variation within a dataset (Phatak, 1993).

3. RESULTS AND DISCUSSIONS

For CCA we divided all of the measured and estimated parameters into five sets. Set-1– proximate and ultimate properties of coals and fractions (moisture, ash content, volatile matter, carbon content, hydrogen content, caking properties of coal measured by Roga Index). Set-2– petrographic composition of coals and fractions (vitrinite, liptinite, inertinite, mineral matter). Set-3– content of seven major elements (elements in concentrations greater than 0.5% in the whole coal) that constitute the ash residue. Set-4– the kinetic parameters of pyrolysis (initial temperatures of kinetic and diffusion regime, final temperatures of kinetic and diffusion regime, pre-exponential factor from Arrhenius equation for kinetic and diffusion regime, activation energy for kinetic regime). Parameters of the reactivity were clustered into fifth class (Set-5).

The results of CCA presented in Table 2 show that the Set-3 explains 42 % of the variance in set variables of reactivity of chars. These indicate and confirm previous results that the nature and distribution of the mineral matter is as important as elemental composition of the ash in determining char reactivity. It is well known, that at the same proportion by mass, different elements have different influence not only on reactivity of chars but change thermal behavior of coal during pyrolysis (Maes et al., 1997) and affects the type of char formed (Cloke and Lester, 1994).

We will now more carefully analyze the data of Table 1. The coals can be regarded as a series of increasing rank (according to reflectance of vitrinite, R_0). Their chars display a broad trend of increasing

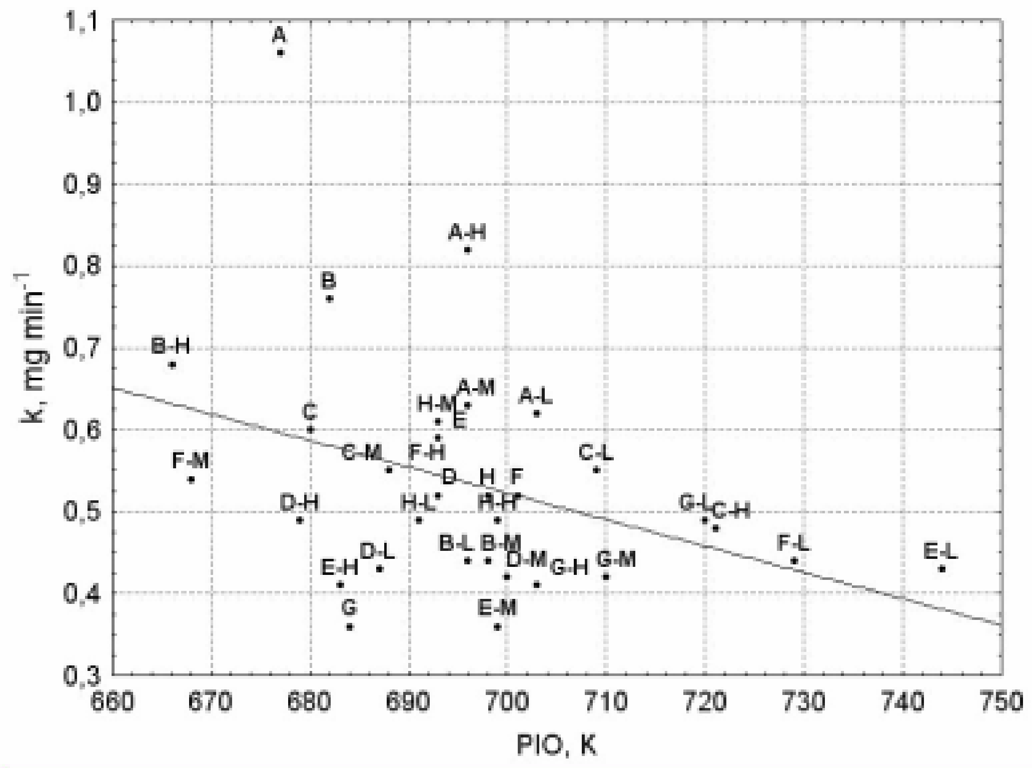

Fig. 1 The scatterplot, point of initial oxidation vs. kinetic constant of combustion for all char samples

Table 2 Results of canonical correlation analysis

Independent variables	Canonical correlation R_c, %	p-significance level (a decreasing index of the reliability of a result)	Total redundancy given the parameters of reactivity of chars, %
Set-1 (6 var.)	53	0.44	17
Set-2 (4 var.)	47	0.34	13
Set-3 (7 var.)	81	0.00	42
Set-4 (7 var.)	57	0.23	24

reactivity with decreasing temperature of initial oxidation (Fig. 1). Decreased reactivity of increasing rank is also observed, a well know fact in char reactivity research. On the other hand, the H anthracite char has higher reactivity then low rank coal. This was attributed to high plasticity of G coal (65 % RI) which gives rise to extinction of the microporosity and therefore the surface area available for oxygen. Chars from A coal with significant low percentage of mineral matter have high reactivity as expected according to the rank. Low rank coals tend to form chars exhibiting isotropic optical textures of high reactivity (Dissel, 1992).

4. CONCLUSIONS

Reactivity of chars cannot be adequately predicted by any single parameter. However, where impurities are considered significant relationships with both ignition and reactivity behavior can be demonstrated. The method we used, canonical correlation analysis, succeeded in identifying how reactivity of coal chars varied across main properties of parent coal. The statistical interpretation of results confirmed the dominant effects of inorganic matter in coals on the reactivity of chars obtained from them.

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