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Changes in the spontaneous combustion tendency of humic coals according to their petrographic composition and physico-chemical properties

Introduction

Currently, due to the worldwide trade of coal and the resulting need for long-term storage of this raw material, the problem of self-heating and self-ignition is particularly important. In addition, the question of self-ignition and activation energy is of importance when taking clean coal technologies such as the gasification process into account. The spontaneous combustion is the tendency of coal, in particular crushed coal, to self-ignition intensified by heat from the decomposition (in moisture) of inclusions of pyrite and chalcopyrite. The studies on the spontaneous combustion of coal have a long history. This research problem has been addressed, among others, by: (Berkowitz and Schein 1951; Bhattacharyya 1972; Falcon 1986; Singh 2013; Thomas and Fariborz 2000; Kataka et al. 2018). The self-heating of coal leading to spontaneous combustion poses a serious threat during its mining, transport and storage (Misra and Singh 1994). According to previous studies, low-rank coals are more prone to self-heating than coals of higher rank; this relationship is not linear and is affected by coal

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type (Clemens et al. 1991; Panigrahi and Sahu 2004), particle size and climate (Misra and Singh 1994). In the case of lower rank coals, a high percentage of reactive macerals (vitrinite and liptinite) may increase the tendency for heating (Lyman 2001). Moreover, the tendency for heating is correlated with higher moisture, net calorific value and higher oxygen content. In addition, the potential of higher-sulfur coals for increased heating stems from the fact that pyrite oxidation is exothermic. The pyrite oxidation was believed to be a major factor in spontaneous combustion; however, it is currently considered to be less important than other oxidizing characteristics. Pyrite contents above 2% are generally required to have any influence. Coal richer in reactive macerals, particularly liptinite and vitrinite, is more prone to self-heating than inertinite-rich macerals (Beamish et al. 2001). Therefore, the main factors affecting the spontaneous combustion of coal include: the rank of coal, oxygen content, the flow rate of the air, particle size, and the moisture content. Special attention should be paid to works focusing on the adsorption of gases released during the self-heating of coal (Cygankiewicz et al. 2006; Zarębska et al. 2012; Dudzińska and Cygankiewicz 2015; Dudzińska 2019). The above authors suggested that the fire gases from the self-heating center can be adsorbed by bituminous coals; this can result in a lower concentration of gas and a change of fire indices. The need to improve the spontaneous combustion indicators contained in the existing standards was also highlighted by Słowik (Słowik 2019), who drew attention to the influence of the temperature of the coal seam.

1. Methods

A total of 29 coal samples from Polish deposits, including 11 low-rank coal from the Polish Lowlands, 16 bituminous coal from the Upper Silesian Coal Basin and Lublin Coal Basin, and one anthracite sample from the Lower Silesian Coal Basin were used in the study. The names of mines or opencasts, age, lithotype and a number of the coal seam sampled are shown in tabular form (Table 1). These samples were taken in the years 2014–2015 by Barbara Bielowicz and Jacek Misiak. Since then all coal samples were stored in AGH in Krakow and therefore they could be used for the analyses, the results of which are included in this paper. The mentioned samples were ground to a grain size of <1 mm and used as material for polished sections made according to the ISO standard. The petrographic examination was carried out in both reflected white and blue light with the use of a Zeiss microscope and in accordance with the PN-ISO 7404-3:2001 standard. The maceral composition of both lignite and bituminous coal was determined according to the ICCP guidelines (Stach et al. 1982; Sýkorová et al. 2005). The macerals from the liptinite group were examined under fluorescent light. The maceral nomenclature for the liptinite group was developed according to Pickel et al. (Pickel et al. 2017). The maceral group content analysis was carried out on 500 equally spaced points on the surface of the polished sections. The proximate analysis included content of: moisture, ash and volatile matter, as well as the gross calorific value determination. The ultimate analysis covered: carbon, hydrogen, nitrogen and sulfur

Table 1. Mine/złoże, age, lithotype and a number of the coal seam sampled

Tabela 1. Kopalnia/złoże, wiek, litotyp i numer opróbowanego pokładu węgla

	Sample	Location, age, lithotype
Lignite	1L	Pątnów (Jóźwin opencast), Middle Miocene (1st seam), detritic
	2L	Pątnów (Jóźwin opencast), Middle Miocene (1st seam), xylitic
	3L	Pątnów (Jóźwin opencast), Middle Miocene (1st seam), detro-xylitic
	4L	Turów, Early Miocen (3rd seam), xylitic
	5L	Turów, Early Miocen (3rd seam), xylo-detritic
	7L	Sieniawa, Early-Middle Miocene (2nd seam), xylo-detritic
	9L	Sieniawa, Early-Middle Miocene (2nd seam), detritic
	10L	Bełchatów, Early Miocen (3rd seam), xylo-detritic
	12L	Bełchatów, Early Miocen (3rd seam), detritic
	13L	Szczerców, Early-Middle Miocene (2nd seam), xylitic
	14L	Szczerców, Early-Middle Miocene (2nd seam), xylo-detritic
Bituminous coal	1B	Janina, Westphalian D (seam 119/2), bright coal
	2B	Janina, Westphalian D (seam 119/2), dull coal
	3B	Janina, Westphalian C (seam 203/2), bright coal
	4B	Janina, Westphalian C (seam 203/2), dull coal
	5B	Bielszowice, Upper Namurian (seam 405/2), bright coal
	6B	Bielszowice Upper Namurian (seam 405/2), dull coal
	7B	Bielszowice, Westphalian A (seam 510), bright coal
	8B	Bielszowice, Westphalian A (seam 510), dull coal
	9B	Bogdanka, Westphalian B (seam 391), bright coal
	10B	Bogdanka, Westphalian B (seam 391), dull coal
	11B	Bogdanka, Westphalian B (seam 381), bright coal
	12B	Bogdanka, Westphalian B (seam 381), dull coal
	15B	Bogdanka, Westphalian B (seam 385/2), bright coal
	16B	Bogdanka, Westphalian B (seam 385/2), dull coal
	17B	Wesoła, Westphalian B (seam 308), bright coal
	18B	Wesoła, Westphalian B (seam 308), dull coal
Coking coal	1CC	Jas-Mos, Westphalian A (seam 510), coking coal
Anthracite	1A	Wałbrzych, Namurian A (seam 672) Anthracite

content determination using a Leco analyzer. All chemical and technological analyses were performed according to ISO standards. The analysis of major oxide composition of ash was determined by ICP-ES analysis in the Bureau Veritas laboratory. The total porosity was determined using an Autopore 9220 mercury porosimeter. Determining the spontaneous combustion indicator (modified Opaliński method) and calculating the activation indicator were carried out according to the Polish standard (PN-G-04558:1993). The two indicators of spontaneous ignition of coal and the activation energy indicator were determined. The analysis of coal susceptibility to spontaneous combustion according to the PN-G-04558:1993 is based on the continuous measurement of the temperature of coal samples in the air stream at 510 K (237°C) and 463 K (190°C). Based on the continuous temperature measurement, the rate of its increment was determined, because, by assumption, it corresponds to the reaction rate. Both indicators of spontaneous ignition of coal were marked as Sz^a and $Sz^{a'}$. On their basis, the energy of activation A was calculated. In order to classify coal based on the susceptibility to spontaneous combustion, the indices Sz^a– the reaction rate determined experimentally at temperature 237°C (°C/min) and A – the activation energy (kJ/mol) were used. Based on these two indicators, coal was classified into four self-combustion groups: V– very easily self-igniting (Sz^a – above 120°C/min), IV – easily self-igniting (Sz^a – 100–120°C/min, A – 34–42 kJ/mol), III – moderately self-igniting (Sz^a – 80–100°C/min, A – 42–46 kJ/mol), II – hardly self-igniting (Sz^a – below 80°C/min, A – 46-67 kJ/mol) and I – very hardly self-igniting (Sz^a – below 80°C/min, A – above67 kJ/mol).

The impact of measured coal parameters on self-igniting and activation energy was determined using Pearson's correlation analysis. All statistical analyses were performed using Statistica 12 software. The parameter distribution was determined using the t-test. In the first step, the correlation for the whole coal series, from lignite to anthracite, was examined. Then, these relationships were analyzed separately for low-, medium- and high-rank coals. The significance of the correlation was p = 0.05. The degree of correlation was determined according to Guilford (Guilford 1965).

2. Results of lignite and bituminous coal analysis

2.1. Proximate and ultimate analysis

The average, minimal and maximal values of the proximate and ultimate analysis of the 11 lignite, 16 bituminous coal, 1 coking coal and 1 antracite coal samples and are summarized in Table 2. The most variable parameter in the tested samples is ash oxide composition. This is associated with various paleoenvironmental and diagenesis conditions under which the coal was formed. The ash content in lignite is highly variable. On the other hand, the moisture and sulfur content are the most variable for medium- and high-rank coal (Table 2).

Table 2. Basic statistics of proximate and ultimate analysis of coal

Tabela 2. Podstawowe statystyki parametrów technologicznych i chemicznych analizowanego węgla

Parameter	All samples				
	Av	Min	Max	Stdv	V (%)
M^{ad} (%)	5.1	0.5	12.0	4.0	79.3
A^{db} (%)	10.7	1.2	46.2	9.4	87.3
V^{daf} (%)	44.0	4.2	64.2	13.8	31.5
S_t^{db} (%)	1.7	0.3	5.3	1.2	74.5
GCV^{daf} (MJ/kg)	30.3	23.9	36.4	4.0	13.2
C^{daf} (%)	74.8	61.8	93.9	9.2	12.3
H^{daf} (%)	5.1	3.2	6.0	0.5	9.8
N^{daf} (%)	1.0	0.1	2.0	0.6	53.7
O^{daf} (%)	17.1	1.6	31.9	9.0	52.3
Total porosity (%)	12.6	1.7	35.9	11.5	91.0
Ash oxide composition (%)					
SiO_2	32.0	7.4	66.8	15.7	49.1
Al_2O_3	19.5	3.0	37.9	10.2	52.6
Fe_2O_3	14.4	2.2	58.9	12.2	84.8
MgO	3.3	0.3	12.4	3.2	98.8
CaO	11.5	1.0	30.0	9.1	79.4
Na_2O	1.8	0.0	12.3	2.9	155.1
K_2O	0.8	0.1	3.1	0.7	87.3
TiO_2	1.0	0.2	2.9	0.6	63.3
P_2O_5	0.9	0.0	4.6	1.3	144.2
MnO	0.1	0.0	0.6	0.1	116.1
Cr_2O_3	0.1	0.0	0.2	0.0	67.7
Parameter	Low-rank coal				
	Av	Min	Max	Stdv	V (%)
M^{ad} (%)	9.1	4.6	12.0	1.9	21.2
A^{db} (%)	13.1	2.3	46.2	12.7	96.5
V^{daf} (%)	57.2	49.4	64.2	3.6	6.3
S_t^{db} (%)	1.9	0.5	3.9	1.2	63.5
GCV^{daf} (MJ/kg)	26.4	23.9	29.2	1.5	5.6
C^{daf} (%)	65.9	61.8	70.7	2.3	3.5
H^{daf} (%)	5.3	4.7	6.0	0.4	7.5
N^{daf} (%)	0.5	0.1	0.9	0.3	55.2
O^{daf} (%)	26.0	21.5	31.9	2.9	11.3
Total porosity (%)	24.6	8.4	35.9	8.3	33.7
Ash oxide composition (%)					
SiO_2	31.8	7.4	66.8	21.0	66.2
Al_2O_3	11.2	3.0	19.0	5.7	50.9
Fe_2O_3	10.3	2.2	21.9	5.7	55.1

Table 2. cont.

Tabela 2. cd.

Parameter	Low-rank coal				
	Av	Min	Max	Stdv	V (%)
MgO	3.1	0.3	11.0	2.9	95.3
CaO	16.9	1.2	30.0	10.1	60.0
Na_2O	1.8	0.0	12.3	4.0	217.3
K_2O	0.5	0.1	1.2	0.4	73.7
TiO_2	1.1	0.3	2.9	0.9	80.6
P_2O_5	0.1	0.0	0.3	0.1	79.5
MnO	0.1	0.0	0.2	0.1	65.4
Cr_2O_3	0.1	0.0	0.2	0.1	75.6
Parameter	Medium- and high-rank coal				
	Av	Min	Max	Stdv	V (%)
M^{ad} (%)	1.9	0.5	5.1	1.6	85.7
A^{db} (%)	8.4	1.2	24.1	5.3	63.7
V^{daf} (%)	33.6	4.2	40.5	8.9	26.6
S_t^{db} (%)	1.4	0.3	5.3	1.2	86.4
GCV^{daf} (MJ/kg)	33.3	29.0	36.4	2.3	6.8
C^{daf} (%)	81.8	74.1	93.9	5.6	6.8
H^{daf} (%)	4.9	3.2	5.4	0.5	10.7
N^{daf} (%)	1.5	1.0	2.0	0.3	21.6
O^{daf} (%)	10.3	1.6	19.3	5.2	50.4
Total porosity (%)	4.1	1.7	10.5	2.5	61.3
Ash oxide composition (%)					
SiO_2	32.4	9.6	50.7	11.9	36.8
Al_2O_3	25.6	8.7	37.9	8.6	33.7
Fe_2O_3	17.7	3.6	58.9	14.9	84.6
MgO	3.5	0.4	12.4	3.5	100.6
CaO	7.2	1.0	19.8	5.9	82.0
Na_2O	2.0	0.4	6.3	2.0	99.7
K_2O	1.0	0.2	3.1	0.8	74.9
TiO_2	1.0	0.2	1.5	0.5	46.9
P_2O_5	1.5	0.0	4.6	1.5	98.9
MnO	0.1	0.0	0.6	0.2	129.4
Cr_2O_3	0.0	0.0	0.1	0.0	39.7

M^{ab} – moisture content, analytical basis, A^{db} – ash content, dry basis, V^{daf} – volatile matter content, dry ash-free basis, S_t^{db} – total sulfur content, dry basis, GCV^{daf} – gross calorific value, dry ash-free basis, C^{daf} – carbon content, dry ash-free basis, H^{daf} – hydrogen content, dry ash-free basis, N^{daf} – nitrogen content, dry ash-free basis, O^{daf} – oxygen content, dry ash-free basis.

Av – average, Min – minimum, Max – maximum, Stdv – standard deviation, V (%) – variability.

2.2. Petrographic analysis

The average, minimum and maximum values of the petrographic analyses of the 29 lignite and bituminous coal samples are presented in Table 3. The examined lignite samples are dominated by the huminite group, which shows the lowest variability. Among the macerals of this group, textinite has the highest variability. In the case of low-rank coals, the most variable components are macerals of the inertinite group, in particular fusinite and semifusinite. The composition of bituminous coal is moderately variable (Table 3). The differences in the content of individual maceral groups are due to the fact that the samples include both bright and dull coal lithotypes.

Table 3. Basic statistics of the petrographic composition (macerals content) of the examined lignites and bituminous coals

Tabela 3. Podstawowa statystyka składu petrograficznego (zawartości macerałów) w badanym węglu brunatnym i kamiennym

Lignite					
Parameter (%)	Av	Min	Max	Stdv	V (%)
Textinite	18.2	1.3	82.7	27.5	150.6
Ulminite	21.3	2.4	55.2	16.2	76.1
Attrinite	20.8	2.0	49.9	13.4	64.4
Densinite	26.7	2.0	46.2	14.3	53.4
Corpohuminite	0.1	0.0	0.8	0.3	200.8
Gelinite	2.3	0.0	8.6	2.5	111.0
Sporinite	0.5	0.2	1.0	0.3	55.9
Cutinite	0.1	0.0	0.3	0.1	61.1
Resinite	1.4	0.5	2.1	0.6	46.3
Suberinite	0.2	0.0	0.6	0.2	104.4
Alginite	0.1	0.0	0.3	0.1	150.0
Liptodetrinite	0.4	0.0	1.1	0.3	91.5
Fusinite	1.8	0.0	14.0	3.8	204.6
Semifusinite	0.1	0.0	0.8	0.2	260.6
Funginite	0.1	0.0	0.5	0.2	246.1
Inertodetrinite	1.1	0.0	4.7	1.5	128.7
Pyrite	0.4	0.0	1.6	0.5	149.8
Carbonates	0.0	0.0	0.4	0.1	360.6
Quartz + Clays	4.0	0.4	10.3	3.0	75.2
Huminite	89.4	73.6	97.1	7.4	8.3
Inertinite	3.2	0.0	19.9	5.3	164.5

Table 3. cont.

Tabela 3. cd.

Lignite					
Parameter (%)	Av	Min	Max	Stdv	V (%)
Liptinite	3.0	1.7	8.5	1.8	59.9
Mineral matter	4.4	0.4	11.1	3.2	72.9
Ro	0.3	0.2	0.3	0.0	6.5
GI	1.7	0.1	4.0	1.3	74.2
Bituminous coal					
Parameter (%)	Av	Min	Max	Stdv	V (%)
Telinite	0.6	0.0	2.2	0.6	104.5
Collotelinite	15.8	2.2	100.0	23.1	146.5
Collodetrinite	43.9	0.0	76.8	19.6	44.7
Vitrodetrinite	1.3	0.0	5.8	1.5	116.9
Corpogelinite	1.2	0.0	3.6	1.1	91.9
Gelinite	1.2	0.0	3.4	1.0	81.2
Macrosporinite	1.4	0.0	7.8	1.8	132.1
Microsporinite	7.8	0.0	16.4	4.7	60.6
Cutinite	1.0	0.0	4.6	1.1	107.1
Resinite	0.7	0.0	2.2	0.6	84.0
Liptodetrinite	2.8	0.0	10.4	3.3	120.1
Fusinite	4.1	0.0	18.5	4.2	101.3
Semifusinite	3.2	0.0	8.6	2.4	75.4
Funginite	4.2	0.0	10.4	3.1	73.1
Macrinite	1.3	0.0	4.0	1.4	114.2
Micrinite	0.3	0.0	1.0	0.3	92.0
Secretinite	0.1	0.0	0.2	0.1	115.0
Inertodetrinite	7.3	0.0	17.6	5.0	67.6
Sulfides	0.7	0.0	3.8	0.9	140.8
Carbonates	0.0	0.0	0.4	0.1	424.3
Clay minerals	1.1	0.0	6.2	1.5	137.3
Vitrinite	64.1	40.0	100.0	17.7	27.6
Inertinite	20.5	0.0	38.2	10.8	52.9
Liptinite	13.7	0.0	28.2	9.6	70.1
Mineral matter	1.8	0.0	7.6	1.8	103.5
Ro	0.7	0.5	2.3	0.4	55.3
GI	6.7	1.8	30.4	7.4	109.3

2.3. Analysis of spontaneous combustion tendency

The spontaneous combustion parameters of lignites and bituminous coals were averaged (Tables 4 and 5). The examined Polish lignites are characterized by lower rates of spontaneous combustion in 237°C (Sz^a) and 190°C ($Sz^{a'}$) and a higher activation energy of carbon oxidation (A) than bituminous coals. The obtained values can be used when determining the spontaneous combustion tendency groups according to the PN-G-04558:1993 standard. On average, the examined lignites represent the first spontaneous combustion tendency group (coals with very low tendency to spontaneous combustion) and the examined bituminous coals – the second group (coals with low tendency to spontaneous combustion). The analysis has shown that the greatest variability among the tested samples was observed in the case of spontaneous combustion at 190°C. However, this variability should be considered as moderate (Mucha 1994).

From all of the examined lignites, the xylitic lignite from the Szczerców deposit, with the lowest rates of spontaneous combustion and the highest activation energy of carbon oxidation, is the least prone to spontaneous combustion. Lignites most susceptible to self-ignition include: xylo-detritic lignite from the Sieniawa deposit, characterized by the highest rate of spontaneous combustion in 237°C, xylitic lignite from the Turów deposit,

Table 4. Basic statistics of spontaneous combustion in 237°C, spontaneous combustion in 190°C, activation energy A and self-ignition group

Tabela 4. Podstawowa statystyka skłonności do samozapłonu w temp. 237°C, skłonności do samozapłonu w temp. 190°C, energii aktywacji A oraz grup samozapalności

Parameter	All samples				
	Av	Min	Max	Stdv	V (%)
Spontaneous combustion in 237°C Sz^a (°C/min)	70.2	16.0	125.0	27.4	39.0
Spontaneous combustion in 190°C $Sz^{a'}$ (°C/min)	15.4	3.0	38.4	9.7	62.8
Activation energy A (kJ/mol)	69.8	47.5	96.8	16.3	23.4
	Low-rank coal				
Spontaneous combustion in 237°C Sz^a (°C/min)	66.1	35.8	92.2	19.8	29.9
Spontaneous combustion in 190°C $Sz^{a'}$ (°C/min)	9.2	3.7	14.7	4.2	45.7
Activation energy A (kJ/mol)	85.4	66.6	95.4	9.5	11.1
	Medium- and high-rank coal				
Spontaneous combustion in 237°C Sz^a (°C/min)	72.7	16.0	125.0	31.4	43.2
Spontaneous combustion in 190°C $Sz^{a'}$ (°C/min)	19.2	3.0	38.4	10.2	53.1
Activation energy A (kJ/mol)	60.2	47.5	96.8	11.4	19.0

Table 5. Spontaneous combustion parameters of the examined coals

Tabela 5. Parametry samozapłonu badanych węgli

Sample	Spontaneous combustion in 237°C Sz^a (°C/min)	Spontaneous combustion in 190°C $Sz^{a'}$ (°C/min)	Activation energy A (kJ/mol)	Self-ignition group
1L	77.90	9.00	90.70	1
2L	40.10	4.30	93.90	1
3L	69.80	8.00	90.90	1
4L	85.70	14.70	74.20	3
5L	78.50	11.50	80.60	1
7L	92.20	13.80	79.80	3
9L	47.60	5.20	93.30	1
10L	70.40	14.40	66.60	2
12L	47.60	5.20	93.30	1
13L	35.80	3.70	95.40	1
14L	81.40	11.80	81.10	3
1B	43.30	9.00	66.00	2
2B	125.00	32.00	57.30	5
3B	118.80	38.40	47.50	4
4B	114.30	31.70	54.00	4
5B	43.10	10.00	61.40	2
6B	41.00	7.40	72.20	1
7B	55.40	13.40	59.70	2
8B	50.40	14.50	52.50	2
9B	78.90	23.60	50.70	2
10B	78.60	20.60	56.30	2
11B	91.50	27.10	51.10	3
12B	101.00	30.60	50.20	4
15B	87.20	23.20	55.70	3
16B	87.20	22.50	57.00	3
17B	67.70	16.30	59.80	2
18B	78.80	16.00	67.10	1
1CC	31.00	6.10	68.50	1
1A	16.00	3.00	96.80	1

which has the highest rate of spontaneous combustion in 190°C and xylo-detritic lignite from the Bełchatów deposit, with the lowest activation energy of carbon oxidation (Table 5).

In the case of bituminous coals and anthracite, the examined anthracite sample 1A is the least susceptible to self-ignition – it has the lowest rate of spontaneous combustion, and the highest activation energy of carbon oxidation. The coals from the Janina mine are the most prone to spontaneous combustion. The dull coal from seam 119/2 has the highest rate of spontaneous combustion in 237°C, while the bright coal from seam 203/3 has the highest rate of spontaneous combustion in 190°C and the lowest activation energy of carbon oxidation (compare Tables 1 and 5).

3. Correlation analysis

The correlation analysis between the ultimate and proximate analysis and the self-ignition indices has been carried out for all samples and separately for lignite and bituminous coal. Pearson's linear correlation coefficients, which are statistically significant at $p = 0.05$, are presented in Table 6. The following interpretation of correlation coefficients was used for r (Guilford 1965):

- (0.00–0.20) weak correlation, the relationship is almost insignificant,
- (<0.20–0.40) low correlation, the relationship is clearly visible,
- (<0.40–0.70) strong correlation, the relationship is clearly visible and small,
- (<0.70–0.90) strong correlation, significant relationship,
- (<0.90–1.00) both correlation and relationship are strong.

Considering the results obtained, it can be stated that more correlations are observed for all rank coal than for lignite and bituminous coal separately. The strongest correlations are observed between measures of the rank of coal (V^{daf}, GCV^{daf}, C^{daf}, O^{daf}) and the activation energy A. An example of a negative moderate relationship is between gross calorific value and activation energy (Fig. 1). It should also be noted that anthracite is characterized by both high activation energy and high gross calorific value. A significant negative relationship between the nitrogen content in coal and the activation energy was also observed (Fig. 2). The total porosity and activation energy are strongly positively correlated (Fig. 3). The oxide composition of ash has a moderate effect on the susceptibility of coal to self-ignition. The Al_2O_3 content in ash has the strongest impact on the activation energy. One of the main objectives of the study was to find the relationship between the petrographic composition and the susceptibility to self-ignition of coal. Based on the results of presented analysis, it can be stated that this relationship is clearly visible. Semifusinite, the total amount of inertinite and liptinite macerals have the greatest effect on Sz^a, $Sz^{a'}$ and A, respectively (Figs. 4–6). These components are moderately negatively correlated with the activation energy. At the same time, the activation energy increases with increasing amount of macerals of the huminite/ /vitrinite group (Fig. 7).

Table 6. Pearson's correlation coefficient for lignite and bituminous coal parameters.
In bold – strong and very strong correlation

Tabela 6. Współczynnik korelacji Pearsona dla parametrów węgla brunatnego i węgla kamiennego.
Pogrubienie – silna i bardzo silna korelacja

	All samples			Lignite			Bituminous coal		
Variable	Sz^{a} (°C/min)	Sz$^{a'}$ (°C/min)	A (kJ/mol)	Sz^{a} (°C/min)	Sz$^{a'}$ (°C/min)	A (kJ/mol)	Sz^{a} (°C/min)	Sz$^{a'}$ (°C/min)	A (kJ/mol)
	Ultimate and proximate analysis								
M^{ad} (%)			0.67		–0.64	0.61	0.53	0.49	
V^{daf} (%)			0.44	–0.60			0.69	0.61	**–0.81**
GCV^{daf} (MJ/kg)			–0.61				–0.59	–0.50	
C^{daf} (%)			–0.52				**–0.70**	–0.61	0.57
H^{daf} (%)							0.48	0.47	**–0.83**
N ^{daf} (%)		0.55	**–0.79**						–0.50
O^{daf}			0.58				0.62	0.53	
Sz^{a} (°C/min)		**0.88**	–0.55		**0.90**	–0.69		**0.97**	**–0.72**
SZ$^{a'}$ (°C/min)	**0.88**		**–0.81**	**0.90**		**–0.93**	**0.97**		**–0.77**
A (kJ/mol)	–0.55	**–0.81**		–0.69	**–0.93**		**–0.72**	**–0.77**	
Total porosity (%)		–0.42	**0.73**						
Al_2O_3		0.56	–0.69						
CaO	–0.48	–0.55	0.55						
K_2O	0.48	0.58	–0.49					0.49	
P_2O_5			–0.47						
	Petrographic analysis								
Telinite			0.39						
Collotelinite									**0.72**
Collodetrinite			–0.56						–0.47
Vitrodetrinite		–0.40	0.62						
Corpogelinite		0.48	–0.51						
Cutinite	0.47	0.62	–0.55				0.53	0.55	
Liptodetrinite	0.42	0.45							
Semifusinite	0.50	**0.70**	–0.69				0.61	0.60	–0.48
Funginite			–0.55						
Inertodetrinite			–0.51						
Huminite/vitrinite (%)		–0.48	0.62						
Inertinite (%)			–0.56						
Liptinite (%)	0.48	0.58	–0.61				0.54		
Mineral matter (%)									
Random reflectance (%)	–0.37						–0.61	–0.55	0.85
Gelification index			–0.46	0.62					

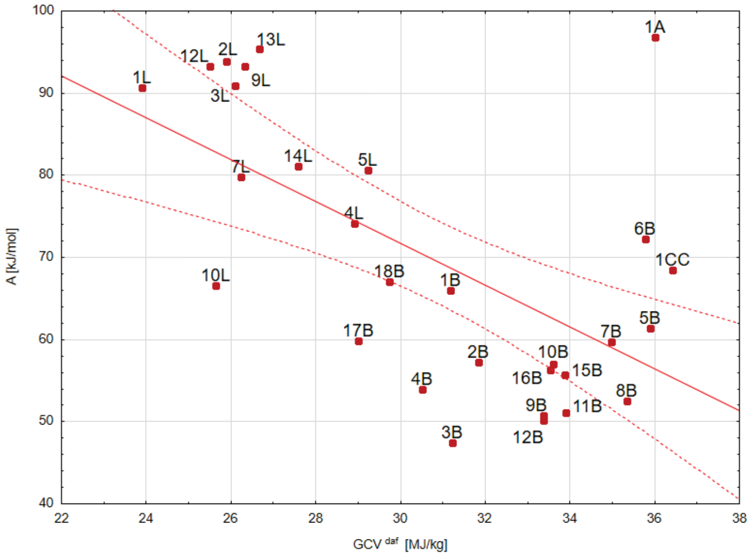

Fig. 1. The relationship between the gross calorific value and the activation energy.
Coal sample numbers as in Table 1

Rys. 1. Zależność między ciepłem spalania a energią aktywacji.
Numery próbek węgla jak w tabeli 1

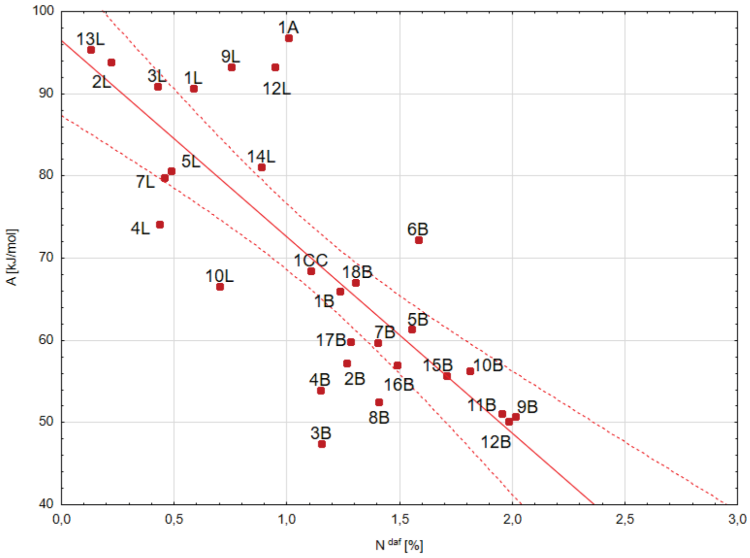

Fig. 2. The relationship between nitrogen content in coal and the activation energy.
Coal sample numbers as in Table 1

Rys. 2. Zależność między zawartością azotu w węglu a energią aktywacji.
Numery próbek węgla jak w tabeli 1

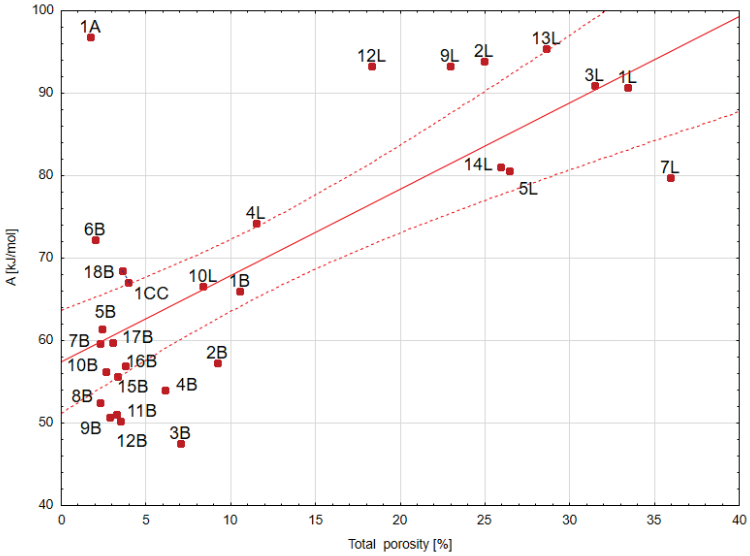

Fig. 3. The relationship between the total porosity in coal and the activation energy.
Coal sample numbers as in Table 1

Rys. 3. Zależność między całkowitą porowatością węgla a energią aktywacji.
Numery próbek węgla jak w tabeli 1

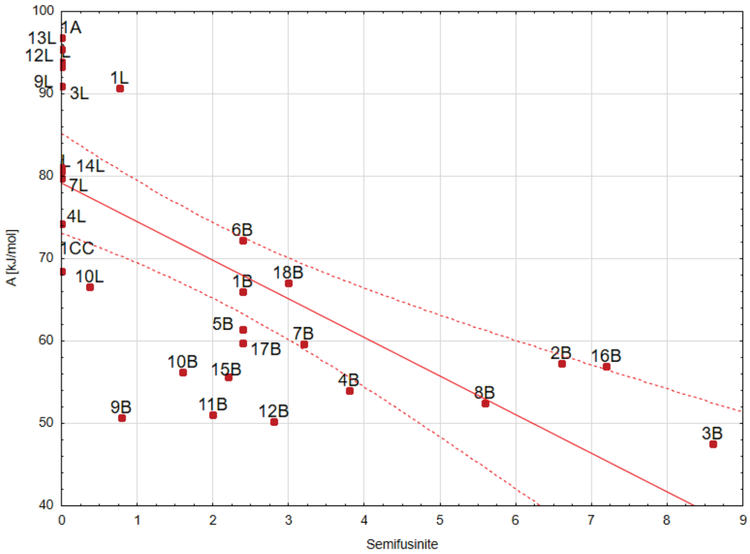

Fig. 4. The relationship between semifusinite content in coal and the activation energy.
Coal sample numbers as in Table 1

Rys. 4. Zależność między zawartością semifuzynitu w węglu a energią aktywacji.
Numery próbek węgla jak w tabeli 1

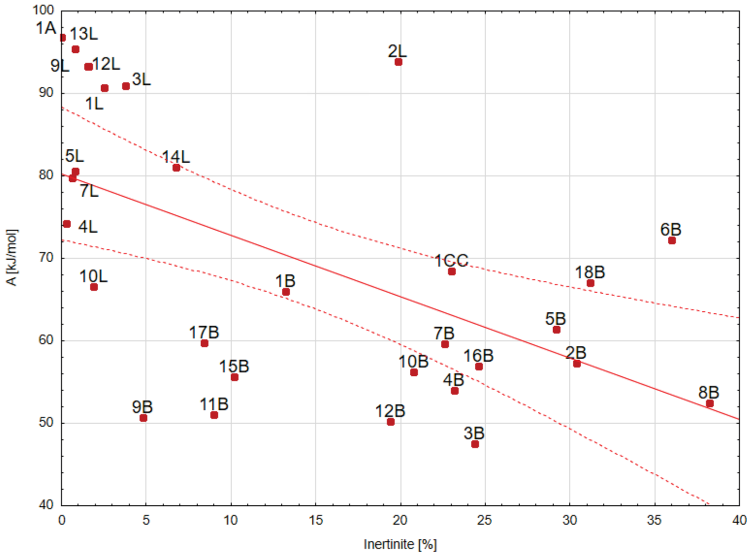

Fig. 5. The relationship between the content of macerals of the inertinite group in coal and the activation energy. Coal sample numbers as in Table 1

Rys. 5. Zależność między zawartością macerałów z grupy inertinitu w węglu a energią aktywacji. Numery próbek węgla jak w tabeli 1

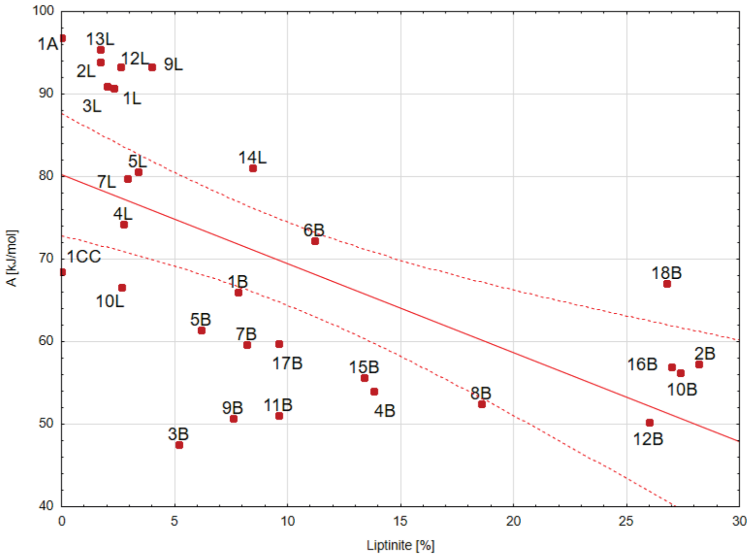

Fig. 6. The relationship between the content of macerals of the liptinite group in coal and the activation energy. Coal sample numbers as in Table 1

Rys. 6. Zależność między zawartością macerałów z grupy liptinitu w węglu a energią aktywacji. Numery próbek węgla jak w tabeli 1

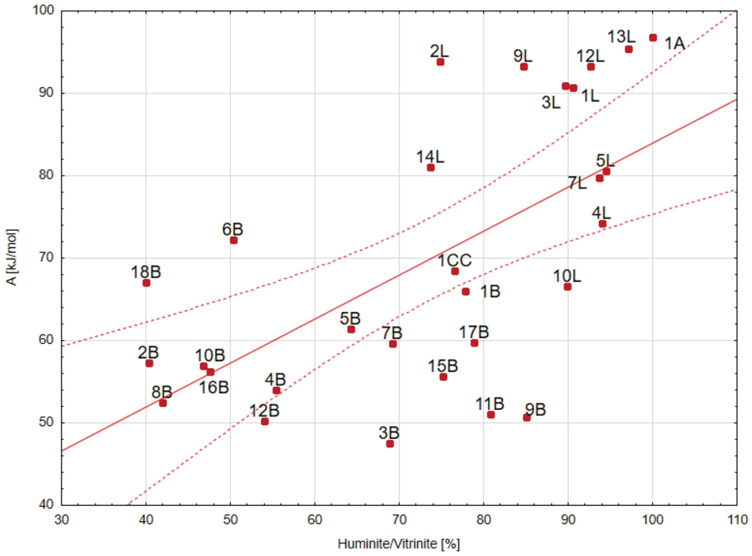

Fig. 7. The relationship between the content of macerals of the huminite/vitrinite group in coal and the activation energy. Coal sample numbers as in Table 1

Rys. 7. Zależność między zawartością macerałów z grupy huminitu/witrynu w węglu a energią aktywacji. Numery próbek węgla jak w tabeli 1

In the case of lignite, high correlations between the chemical, technological, petrographic properties and the self-combustion parameters are rare. Moderate correlations were observed only in the case of moisture and volatile matter content. Moisture (M^{ad}) correlates positively with the activation energy of carbon oxidation (A) and negatively with rates of spontaneous combustion in 190°C ($Sz^{a'}$). This suggests that lignite with higher moisture content has a lower tendency of self-combustion. A significant negative correlation between the volatile matter content (V^{daf}) and the rate of spontaneous combustion in 237°C (Sz^{a}) has been observed. This suggests that in the case of lignite, the rate of spontaneous combustion decreases with increasing the volatile matter content (Table 6).

In the case of bituminous coals and anthracite, moderate and high correlations were observed between all of the self-combustion parameters and the volatile matter content (V^{daf}). The moderate positive correlations with the rates of spontaneous combustion (Sz^{a}, $Sz^{a'}$) and the high negative correlation with the activation energy of carbon oxidation (A) suggest that the bituminous coal tendency to self-combustion increases with the increasing volatile matter content. A similar dependence was observed in the case of the hydrogen (H^{daf}) and oxygen (O^{daf}) content. However, some of the correlations between them and the self-combustion parameters were moderate. Other important correlations were observed in the case of the moisture content and in the case of carbon content (C^{daf}). The values of Pearson's correlation coefficient suggest that higher moisture contributes to the higher tendency to self-combustion and that a high carbon content is the reason for lower tendency of self-combustion. The relationship between carbon content and self-ignition is also consistent with the correlation between the self-combustion parameters and the reflectance (Ro) – another parameter of the degree of coalification. Both the C^{daf} and Ro correlation suggest that in the case of bituminous coals, the coal with a higher degree of coalification is less prone to self-combustion. Taking into account the correlations with the petrographic composition, the most noticeable are those concerning the content of macerals from the collotelinite, semifusinite and liptinite groups. The collotelinite content has a high, positive correlation with the activation energy of carbon oxidation, which suggests that the high content of this maceral is related to the lower tendency to self-combustion. Semifusinite has moderate to high positive correlations with the rates of spontaneous combustion and a moderate, negative correlation with the the activation energy of carbon oxidation. In this case, the results suggest that the high semifusinite content is responsible for the higher tendency to self-combustion. The situation is similar in the case of macerals from the liptinite group, where their higher content contributes to the higher tendency to self-combustion (Table 6).

Comparing the correlation results obtained for lignite and bituminous coal, it was noted that the most noticeable correlations were reverse. This means that the correlation between the activation energy of carbon oxidation (A) and volatile matter content (V^{daf}) was positive in the case of lignite and negative in the case of bituminous coal. Those differences may result from the different molecular composition of lignite and bituminous coal.

In the case of lignite, the increase of carbon content is the reason for its higher tendency to self-ignition. Carbon in lignite is mostly connected by aliphatic bonds. Their high concentration in coals contributes to their instability and susceptibility to oxidation and self-heating. In the case of different bituminous coals, the content of aliphatic bonds decreases with the degree of coalification, which may explain the observed correlation between the decreasing tendency to spontaneous combustion and the increasing carbon content (Berkowitz and Schein 1951; Choudhury et al. 2016).

Numerous authors have suggested that the susceptibility to spontaneous combustion increases with the increase in the moisture content (Ciesielczuk et al. 2013; Wen et al. 2015; Choudhury et al. 2016). This is consistent with the correlation results for bituminous coal, but not for lignite. However, some researchers believe that the high moisture content may inhibit the self-heating process (Bhattacharyya 1972; Choudhury et al. 2016). In addition, a study by Xu et al. (Xu et al. 2013) has shown that the critical moisture content in lignite, when it is the most prone to self-ignition, is 25% (Xu and He 2013). The obtained correlation results suggest that in the case of lignite the lower tendency to self-combustion decreases with the increase of moisture content. In the examined samples, the average total moisture content was 18.59%, that is, lower than the critical moisture content. In this case, it can be said that the moisture inhibits the self-ignition.

Numerous authors have noted that the petrographic composition affects the tendency of coal to spontaneous combustion. Simply put, the reactive macerals from the vitrinite and liptinite groups are the reason for the higher susceptibility to self-ignition (Falcon 1986; Chakravorty and Kolada 1988; Misra and Singh 1994; Mastalerz et al. 2011; Misz-Kennan and Fabiańska 2011) i.e., the maceral and microlithotype composition of the organic matter and its rank. Alteration of wastes also depends on the heating history, i.e., the rate of heating, final heating temperature, duration of heating, and the degree of air access. Although air is probably necessary to initiate and drive the heating processes, these usually take place under relatively oxygen depleted conditions. With slow heating, color of organic matter particles changes, irregular cracks and oxidation rims develop around edges and cracks, and bitumen is expelled. As a result, massive and detritic isotropic and strongly altered organic matter forms. On the other hand, higher heating rates cause the formation of devolatilization pores, oxidation rims around these pores and along cracks, vitrinite-bands-mantling particles, and bitumen expulsions. Organic compounds generated from the wastes include n-alkanes, iso-alkanes, alkylcyclohexanes, acyclic isoprenoids, mainly pristane, phytane and, in some cases, farnesane, sesquiterpanes, tri- and tetracyclic diterpanes, tri- and pentacyclic triterpanes, and steranes, polycyclic aromatic hydrocarbons (mostly with two- to five rings, rarely six rings. The correlation analysis of bituminous coal also suggests the influence of liptinite content on spontaneous combustion parameters. However, in the case of vitrinite, no significant correlation has been observed. Only collotelinite content correlates positively with the activation energy of carbon oxidation, which suggests that this maceral makes coal less prone to self-ignition. However, this observation may be biased by the results obtained for anthracite, which consisted of collotelinite only, and because of the fact that its molecular composition is the least susceptible to spontaneous combustion of all of the examined coals. The correlation analysis also suggests that the increase of the semifusinite content makes coal more prone to self-ignition. This observation may be connected to the reactive inertinite, which is represented by low-reflectance micrinite and semifusinite (Kruszewska 1989; Kruszewska and Misz 1999). In the case of vitrinite and liptinite, their impact on the combustion tendency of coal is related to their reactivity. The obtained correlation results may suggest that the situation is similar in the case of semifusinite.

Conclusions

The results of analyses included in this paper partially confirmed the investigation results of other researchers. It should be noted that previous studies have not taken the lithotype of coal into account. Generally, it can be stated that there is no data in the literature on petrography of lignite. The current studies have shown that the mixed lithotypes (xylo-detritic and detro-xylitic coal) have the highest tendency of spontaneous combustion. The correlation relationships between ultimate and proximate analysis, the energy of activation and self-ignition are more pronounced in bituminous coal. The influence of moisture, volatile matter content, carbon and hydrogen content on the tendency to self-combustion and activation energy is clearly visible. This is observed both for lignite and bituminous coal.

In addition, it has been shown that the tendency to self-heating decreases with the increasing degree of coalification. No relationship between the pyrite content and the tendency to self-ignition has been confirmed. The obtained results are particularly important in the context of gasification. In the case of underground gasification, it is particularly important to prevent underground fires in the voids after gasification. This is due to the occurrence of the unreacted, dried coal with a low volatile matter content. In the context of the research results presented in this paper, it can be concluded that the ungasified coal left in the voids has a lower tendency to self-combustion than coal before the gasification process.

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CHANGES IN THE SPONTANEOUS COMBUSTION TENDENCY OF HUMIC COALS ACCORDING TO THEIR PETROGRAPHIC COMPOSITION AND PHYSICO-CHEMICAL PROPERTIES

Keywords

coal, spontaneous combustion, self-ignition, activation energy, petrography,

Abstract

The article presents the analysis of the correlation between the self-ignition parameters and the ultimate and proximate analysis, as well as the petrographic properties of Polish lignite, sub-bituminous coal, bituminous coal and anthracite. The following coal properties were determined: the moisture, ash content, volatile matter and sulfur content, gross calorific value, net calorific value, C, O, N and H contents, total porosity, ash oxide composition, rates of spontaneous combustion in 237°C and 190°C, and activation energy. During the petrographic analysis, maceral composition and random reflectance were determined. To determine the linear correlation between the self-ignition parameters and the analyzed coal properties, the Pearson correlation coefficient was calculated. The results show that there is no strong linear correlation between the lignite tendency to self-ignition and its petrographic properties. However, a strong negative correlation between the rate of spontaneous combustion and moisture and volatile matter content was observed. In the case of bituminous coal, strong correlations between self-combustion parameters and various coal properties were confirmed. The most noteworthy are the correlations between self-ignition parameters and the maceral composition, that is, between the content of macerals of the inertinite group in coal and content of macerals of the huminite/vitrinite group. The obtained results suggest that the spontaneous combustion tendency of coal increases with the increasing content of semifusinite and liptinite.

WPŁYW PARAMETRÓW FIZYKO-CHEMICZNYCH I PETROGRAFICZNYCH WĘGLA HUMUSOWEGO NA JEGO SKŁONNOŚĆ DO SAMOZAPŁONU

Słowa kluczowe

węgiel, samozapłon, samozagrzewanie, energia aktywacji, petrografia

Streszczenie

W artykule przedstawiono analizę korelacji między parametrami samozapłonu a analizą technologiczną i chemiczną oraz właściwościami petrograficznymi polskiego węgla brunatnego, węgla kamiennego i antracytu. Określono następujące właściwości węgla: wilgotność, zawartość popiołu, zawartość części lotnych i siarki, wartość opałową, ciepło spalania, zawartość C, O, N i H, całkowitą porowatość, skład tlenkowy popiołu, wskaźniki samozapłonu w temperaturach 237 i 190°C oraz energię aktywacji. Podczas analizy petrograficznej określono skład petrograficzny i współczynnik odbicia. W celu określenia liniowej korelacji między parametrami samozapłonu a analizowanymi właściwościami węgla obliczono współczynnik korelacji Pearsona. Uzyskane wyniki pokazują,

że nie ma silnej korelacji liniowej między tendencją węgla do samozapłonu a jego właściwościami petrograficznymi. Zaobserwowano jednak silną ujemną korelację między samozapłonem a wilgotnością i zawartością substancji lotnych. W przypadku węgla kamiennego potwierdzono silne korelacje między parametrami samozapłonu a różnymi właściwościami węgla. Najbardziej godne uwagi są korelacje między parametrami samozapłonu a składem petrograficznym, tj. pomiędzy zawartością macerałów grupy inertynitu w węglu oraz zawartością macerałów grupy huminitu/witrynitu w węglu. Uzyskane wyniki sugerują, że tendencja do samozapłonu węgla rośnie wraz ze wzrostem zawartości semifuzynitu i liptynitu.