



Relationships between quality of coals, resulting cokes, and micro-Raman spectral characteristics of these cokes



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ABSTRACT

The research was carried out on 18 single-coal cokes obtained in semi-industrial conditions from different parent coals ($R_r = 0.84\text{--}1.43\%$). Coke microstructure was investigated by micro-Raman spectroscopy with application of the streamline mode. The obtained Raman spectra are typical for poorly organized carbonaceous material. Correlations were found between the volatile matter content, all maceral reflectance scan, mean random vitrinite reflectance and carbon content of the parent coals, and the full width in half maximum (FWHM) of the D2 and G bands in the Raman spectra of the resulting cokes. There is a non-linear relationship between dilatation and the G band FWHM. Coke reactivity index (CRI) and coke strength after reaction (CSR) are correlated with the D2, G and D4 band FWHMs. Based on the G and D2 band widths, it is possible to predict roughly the CSR and CRI values of cokes.

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1. Introduction

Coke microstructure was studied by means of transmission electron microscopy (TEM) (Duber et al., 2002; Feng et al., 2002, 2003; Oberlin and Oberlin, 1983; Pusz et al., 2010; Rouzaud, 1990; Rouzaud and Oberlin, 1989; Sharma et al., 2001) and X-ray diffraction analysis (XRD) (Feng et al., 2002, 2003; Feret, 1998; Gupta et al., 2005, 2013; Johnson et al., 1986; Kashiwaya and Ishii, 1991; Kawakami et al., 2006; Matsuoka et al., 2008; Oberlin and Oberlin, 1983; Oya et al., 1983; Sato et al., 1998; Smędowski et al., 2011). Important conclusions were also drawn from reflectance measurements (Duber et al., 2002; Pusz and Buszko, 2012; Pusz et al., 2009, 2010; Rouzaud and Oberlin, 1989). A review of coke structural studies with the use of these methods was made by Li et al. (2014).

More rarely, coke was investigated by Raman spectroscopy, which is a common method of microstructural examination of different carbonaceous materials, providing information both about the ordered ("crystalline") and amorphous phase (Bar-Ziv et al., 2000; Bernard et al., 2010; Dong et al., 2007, 2009; Green et al., 1983; Johnson et al., 1986; Kawakami et al., 2005, 2006; Mochida et al., 1984; Rantitsch et al., 2014; Smędowski and Krzesińska, 2013; Smędowski et al., 2011; Urban et al., 2003). Most of these studies focused on microstructural alteration of heat-treated cokes (Bar-Ziv et al., 2000; Bernard et al., 2010;

Dong et al., 2007, 2009; Johnson et al., 1986; Kawakami et al., 2005, 2006; Urban et al., 2003). Only in some of them relationships between quality of cokes and their Raman spectral characteristics were found. Results presented by Smędowski et al. (2011) as well as Smędowski and Krzesińska (2013) indicated that coke reactivity index (CRI) and coke strength after reaction (CSR) might be related to Raman spectral parameters. In recent work, by Rantitsch et al. (2014), three basic types of Raman spectra of coke were discriminated. Their predominance in a bulk sample predicts roughly the coke quality.

However, there have been no studies on the problem, based on a considerable number of samples. Works, in which Raman spectral parameters of cokes are related to the properties of the parent coals are missing. The aims of this study were to:

- (1) examine microstructure of cokes derived from different parent coals by means of Raman spectroscopy,
- (2) analyze how the physical and chemical properties of the parent coals and resulting cokes are related to the Raman spectral characteristics of these cokes.

2. Methods

The research was carried out on 18 samples of parent coals and resulting single-coal cokes. The coal samples were carbonized in the Enviform Laboratory in Trinec (Czech Republic) with the use of the

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KARBOTEST, which is a patented installation, ensuring the same atmosphere and coking conditions during heat-treatment as in a cokemaking oven. Each coal sample equal 5 kg (the amount necessary for further coke quality testing) with the grain size ≤ 3 mm was placed in a steel retort, which was then put into hot oven. Coal was carbonized for 3.5 h, until the temperature of 950 °C was reached. Cokes were kept in the final temperature for 30 min, and then cooled down to the temperature of -50 °C. Similar installation and coking conditions were applied by Puzs and Buszko (2012).

The coals ($R_r = 0.84$ – 1.43%) were collected mostly in the Upper Silesian Coal Basin of Poland and Czech Republic (14 samples) from Upper Carboniferous (Pennsylvanian) deposits. Individual coal samples came from the Blue Creek, Keystone and Shoal Creek deposits in the USA (Pennsylvanian), and from Columbia (Upper Cretaceous/Paleogene). Selected physical, chemical-technological and petrographic properties of the coals are summarized in Table 1. Physical and chemical properties of cokes obtained from these coals are reported in Table 2. The analyses were performed in the Enviform Laboratory in Trinec and in Centralne Laboratorium Pomiarowo-Badawcze in Jastrzębie-Zdrój, according to the ISO standards. The CRI and CSR analyses were executed in agreement with ISO 18894 (2006) standard.

Micro-Raman spectral analysis was carried out using a Renishaw inVia spectrometer (excitation line $\lambda_0 = 514$ nm). The streamline mode was applied. It collects spectra from a strip, covering larger area ($10 \mu\text{m} \times 2 \mu\text{m}$, in this study) than in typical punctual measurements. The measurements in each sample were performed on 30 randomly chosen grains of coke crushed to < 1 mm in size. This ensures that the heterogeneity of a coke sample is taken into account, providing averaged estimate. The initial spectra were recorded within the range of 800 – 2000 cm^{-1} (Fig. 1). The laser power on a sample surface was controlled at 5 mW. The spectrometer was calibrated using an internal silicon standard (peak position – 520 cm^{-1}). During each measurement 10 acquisitions of 5 s were co-added. Then the spectra gained from all 30 grains were summed up, and a final spectrum, representative for a whole coke sample, was obtained and analyzed. Curve-fitting procedure was performed within the spectral range of 1000 – 1800 cm^{-1} , with the use of GRAMS 32 software, following the method presented by Sadezky et al. (2005), which is frequently applied in examination of cokes, chars and carbonized coal maceral concentrates. Four Lorentz curves (D2, G, D1 and D4 bands) and one Gaussian curve (D3 band) were used (Fig. 2). The band assignments were discussed in detail by Beny-Bassez and Rouzaud (1985), Beyssac et al. (2003), Cuesta et al. (1994),

Table 2
Selected physical and chemical properties of the studied cokes.

Sample	W ^a %	A ^a %	V ^{daf} %	C ^{daf} %	H ^{daf} %	N ^{daf} %	O ^{daf} %	S ^a %	CRI	CSR
1	0.32	12.60	1.00	98.52	0.54	0.52	0.42	0.6	40.10	35.20
2	0.14	9.90	0.83	95.25	0.48	0.61	3.66	0.51	37.60	54.10
3	0.13	7.36	1.19	97.57	0.66	1.03	0.74	0.47	54.70	37.20
4	1.17	6.10	2.80	93.60	3.14	1.44	1.81	0.64	73.70	11.70
5	0.25	9.20	0.94	98.54	0.16	1.06	0.24	0.64	43.30	45.20
6	0.11	7.10	1.28	98.19	0.22	1.21	0.38	0.52	53.70	42.50
7	0.41	5.14	0.98	97.34	0.54	0.86	1.26	0.45	66.20	35.80
8	0.06	12.50	1.02	97.97	0.44	0.93	0.66	0.58	34.00	46.80
9	0.12	5.90	1.40	97.33	0.58	1.07	1.03	0.48	53.70	39.00
10	0.40	10.80	0.96	97.84	0.45	1.08	0.63	0.8	50.00	36.80
11	0.08	9.70	0.90	97.81	0.29	1.28	0.61	0.56	28.80	58.60
12	0.10	7.60	1.10	98.60	0.40	0.96	0.03	0.62	27.70	58.40
13	0.25	8.20	1.12	98.00	0.46	1.25	0.29	0.53	39.80	55.80
14	1.05	8.50	0.91	97.95	0.60	1.26	0.19	0.51	21.20	71.30
15	0.10	10.50	0.94	97.96	0.12	1.13	0.79	0.59	27.80	65.40
16	0.12	8.10	1.03	98.26	0.44	1.27	0.03	0.59	29.60	61.80
17	0.09	7.08	0.95	98.11	0.61	0.96	0.32	0.48	44.90	50.30
18	0.24	9.55	0.78	97.58	0.51	1.10	0.80	0.44	41.50	45.20

Explanations: W^a – moisture content, A^a – ash content, V^{daf} – volatile matter content, C^{daf} – carbon content, H^{daf} – hydrogen content, N^{daf} – nitrogen content, O^{daf} – oxygen content (by difference), S^a – sulphur content, CRI – coke reactivity index, CSR – coke strength after reaction.

Green et al. (1983), Jawhari et al. (1995), Nemanich and Solin (1979), Sadezky et al. (2005), Schwan et al. (1996), Tuinstra and Koenig (1970), and the followers. They were also summarized by Morga (2011a, 2011b). Goodness of fit was checked by χ^2 test. Based on that, position and FWHM (full width at half maximum) of the Raman bands were found (Table 3). Fitting errors were also given. The relative band intensities I_{D1}/I_G and I_{D2}/I_G (band height ratios) were determined.

3. Results and discussion

The spectra (Fig. 1) show the occurrence of five bands: D2, G, D3, D1 and D4. The G band ($\sim 1595 \text{ cm}^{-1}$) corresponds to the stretching vibration mode with E_{2g} symmetry in the graphite aromatic layers (Nemanich and Solin, 1979; Tuinstra and Koenig, 1970). The D2 band ($\sim 1620 \text{ cm}^{-1}$) makes a shoulder on the G band, and it is also assigned to a graphitic lattice mode E_{2g} (Cuesta et al., 1994; Green et al., 1983). Its intensity decreases with increasing degree of organization (Beyssac et al., 2003). The D3 band ($\sim 1520 \text{ cm}^{-1}$) originates due to interstitial

Table 1
Selected optical, chemical-technological and petrographic properties of the parent coals.

Sample	R _r %	R _{scan} %	W ^a %	A ^a %	V ^{daf} %	b %	SI	C ^{daf} %	H ^{daf} %	N ^{daf} %	O ^{daf} %	S ^a %	V %	L %	I %	MM %
1 (US)	0.84	0.88	1.94	8.21	36.50	21	6.0	84.46	5.27	1.75	8.52	0.72	59.0	12.0	24.6	4.4
2 (US)	0.85	0.92	1.59	7.59	33.30	18	7.0	84.81	4.80	1.51	8.89	0.59	55.6	11.2	30.0	3.2
3 (US)	0.86	0.95	1.78	6.05	32.88	2	5.0	86.22	5.03	1.53	7.22	0.57	52.6	14.0	31.0	2.4
4 (US)	0.86	0.92	1.56	5.67	34.90	25	7.0	86.19	5.11	1.57	7.13	0.81	50.2	16.0	30.8	3.0
5 (US)	0.86	0.85	1.22	6.95	30.98	25	6.0	86.54	5.11	1.55	6.81	0.58	58.0	7.6	29.4	5.0
6 (US)	0.86	0.94	0.42	7.14	35.60	5	6.0	85.97	5.17	1.50	7.36	0.44	53.4	11.0	32.4	3.2
7 (US)	0.92	1.14	1.29	3.76	29.99	0	4.5	87.06	4.62	1.45	6.87	0.34	33.8	8.6	56.6	1.0
8 (SC)	1.04	1.04	1.54	9.16	31.30	143	8.0	85.01	4.76	1.76	8.46	0.68	66.8	8.4	23.4	1.4
9 (US)	1.05	1.32	0.74	4.99	25.60	66	5.5	89.46	4.67	1.39	4.47	0.36	27.8	13.4	57.6	1.2
10 (KE)	1.06	1.20	0.66	7.59	24.90	148	7.5	88.24	4.67	1.39	5.70	0.99	73.8	0.2	22.2	3.8
11 (US)	1.06	1.11	0.98	8.19	27.30	145	7.5	87.24	4.83	1.54	6.38	0.75	68.2	5.0	20.2	6.6
12 (CO)	1.08	1.11	0.82	6.65	29.80	71	7.0	89.38	4.36	1.47	4.79	0.80	55.0	3.0	36.4	5.6
13 (US)	1.14	1.37	0.48	7.42	24.50	47	4.0	87.47	4.74	1.48	6.31	0.49	48.2	4.2	41.0	6.8
14 (US)	1.22	1.42	0.79	6.05	24.71	130	7.5	88.82	4.83	1.51	4.84	0.61	66.2	2.0	25.2	6.6
15 (BC)	1.31	1.50	0.67	9.26	21.78	107	7.5	89.60	4.67	1.73	3.99	0.64	68.6	0.2	25.2	6.0
16 (US)	1.33	1.53	0.64	6.06	22.88	82	8.0	90.42	4.78	1.31	3.49	0.69	57.4	0.6	35.2	6.8
17 (US)	1.42	1.50	0.76	5.67	24.76	65	6.0	89.34	4.80	1.39	4.47	0.51	40.4	11.6	45.2	2.8
18 (US)	1.43	1.45	0.99	5.96	27.94	50	6.0	87.59	4.91	1.42	6.08	0.40	70.0	3.4	25.8	0.8

Explanations: US – Upper Silesian Coal Basin (Polish and Czech part), SC – Shoal Creek deposit (USA), KE – Keystone deposit (USA), CO – Colombian coal, BC – Blue Creek deposit (USA); R_r – mean random vitrinite reflectance, R_{scan} – all maceral reflectance scan, W^a – moisture content, A^a – ash content, V^{daf} – volatile matter content, b – dilatation, SI – Swelling Index, C^{daf} – carbon content, H^{daf} – hydrogen content, N^{daf} – nitrogen content, O^{daf} – oxygen content (by difference), S^a – sulphur content, V – vitrinite content, L – liptinite content, I – inertinite content, MM – mineral matter content.

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