



Full Length Article

Char structure dependence on formation enthalpy of parent coal

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ABSTRACT

The aim of this work was to investigate char structure dependency on parent coal rank expressed by the formation enthalpy. For this purpose, a detailed characterization of eleven char samples obtained under the same pyrolysis conditions was performed. The porous structure was investigated in terms of micro-, meso- and macropores by employing nitrogen adsorption at 77 K, carbon dioxide adsorption at 273 K and mercury intrusion porosimetry. In order to assess both the carbon crystalline structure and degree of structure organization, the X-ray diffraction and Raman spectroscopy techniques were employed as well. The found correlations revealed a strong linear dependency of aromaticity index and char rank parameters from the formation enthalpy of parent coal. Other char parameters, like micropore and macropore surface area, average crystalline sizes and band area ratio from Raman spectroscopy demonstrate weaker correlation but still the results suggest a valid relationship with formation enthalpy of parent coal.

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1. Introduction

It is generally accepted that coal will still play a crucial role in world's energy mix for the next decades. So far, coal has been consumed to supply energy mostly by combustion, but it can be exploited to generate energy and produce chemicals and fuels through gasification processes as well. One of the advanced clean coal technologies incorporates CO₂ as a co-gasifying agent enhancing course of the reverse Boudouard-Bell reaction. The CO₂ acts as a carbon and oxygen donor allowing for increasing the syngas production economy as compared to conventional gasification technologies [1]. This technology is currently being investigated in a 1 MW_{th} circulating fluidized bed reactor at Institute for Chemical Processing of Coal.

The coal subjected to gasification process undergoes devolatilization followed by the gasification with the latter taking place on the surface of a nascent char. The formation of char involves major transformations within the organic matter and results in decreasing reactivity of residual char. In consequence, the char gasification step is considered rate-determining for overall process. The reactivity loss is partly associated with ordering of carbon crystalline structure [2–4] and, to a lesser extent, changing the phase composition of the inherent mineral matter due to partial oxidation or reduction, sublimation of metals and oxides [5–6], and deactivation during partial sintering [7].

Numerous instrumental techniques should be employed in order to assess the structure of carbonaceous material. The porous structure characteristics can be examined by using of many different techniques, including physisorption, mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). The carbon crystalline structure can be characterized by such advanced methods like X-ray diffraction (XRD) and Raman spectroscopy.

During the heterogeneous reactions between gasifying agents and carbon, the reaction rate is strictly connected with the accessible surface area of the solid fuel [8–13]. The type of porosity (namely, existence and properties of micro-, meso- and macropores) will influence the surface area of resultant char [14–15]. Thus, the knowledge concerning the properties of micro-, meso- and macropores is fundamental for evaluating the porous structure as a whole. This can be done assessing the data from both N₂ and CO₂ adsorption isotherms and mercury intrusion porosimetry, covering together the very broad range of pore sizes. The initial textural properties of the solid will influence the reactivity behavior during gasification [15].

The crystalline structure of different carbonaceous materials can be quantitatively obtained by employing the X-ray diffraction which is the most commonly used technique to examine the degree of aromaticity and the crystallite features [14,16–17].

Raman spectroscopy was found as a viable tool for evaluating the structural properties of highly disordered carbonaceous materials by many investigators [18–21] due to its high sensitivity to crystalline, molecular and amorphous structure and minimal influence of mineral constituents of the inorganic matter.

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The aforementioned structure-based parameters of chars are considered as being influenced mainly by one factor, explicitly, the rank of parent coal. The degree of coal metamorphism determines its structure in terms of pore characteristics, and both crystalline and molecular arrangement. However, the classification of coals by rank is still under discussion in terms which parameters should be taken into account. Moreover, the char-like forms of carbonaceous material, which are sometimes abundant in organic-rich rocks, were included in the specially introduced classification system as natural coke or natural char [22]. According to the paper of Ściążko [23], the existing classification systems are not consistent and the technological needs are not directly addressed. Incorporating the thermodynamical parameter being the enthalpy of formation, allows for better characterization of solid fuel in terms of its potential for further processing.

Since the gasification reactivity is of primary importance to the process, any factors influencing the char reactivity will have essential implications for the gasifier operation. Thus, the knowledge on char structure and its dependency from parent coal rank (expressed by the formation enthalpy) is essential for rational predicting the char reactivity behavior. Therefore, the objective of this study is to assess the structure of chars obtained under the same pyrolysis conditions from coals of differed origin and to find a structure dependency from the parent coal rank.

2. Experimental

2.1. Parent coals characteristics

Eleven coal samples, four lignites, two sub-bituminous and five high volatile bituminous were selected for the studies. The samples

were obtained from Polish mines, with particle sizes ranging from 1 to 50 mm. The thorough characterization of parent coal samples is given in Table 1 where the data regarding proximate, ultimate analyses are gathered together with the heating values, chemical composition of ash and huminite/vitrinite reflectance values. The results show that the studied samples varied significantly with their composition. The high volatile bituminous Budryk coal (which is commercially used as a coalblend component for caking processes) distinguishes itself with highest content of ash of nearly 25 wt. %, while lower rank Turów lignite and Wieczorek-2 bituminous coal have the lowest content of mineral matter and the ash content yielding of 8.1 and 3 wt. %, respectively.

2.2. Formation enthalpy of parent coals

The parent coals were characterized also in terms of their formation enthalpy, $\Delta_f H^\circ$. As reported by Ściążko [23], the rank of a given coal can be expressed by its thermodynamical potential which value is, indeed, a reflection of time and temperature conditions occurring during processes of geological formations of the organic matter [23]. The formation enthalpy can be calculated by using of formula introduced by Ściążko [23–25] combining the thermodynamic heat of combustion and a corrective parameter, f :

$$\Delta_f H^\circ = \Delta_c H^\circ (1 - f) \quad (1)$$

where: $\Delta_c H^\circ$ denotes the specific heat of combustion calculated from empirical correlations involving the mass concentration of carbon, hydrogen and organic form of sulfur to be combusted into CO₂, water and SO₂, respectively; and f is the corrective parameter defined by Eq. (2):

Table 1
The results of analyses of the parent coals.

Sample origin	LigB "Bełchatów-1"	LigB "Sieniawa"	LigB "Bełchatów-2"	LigA "Turów"	SubB "Janina"	SubA "Piast"	hVcb "Sobieski"	hVcb "Wieczorek-1"	hVab "Budryk"	hVcb "Bogdanka"	hVab "Wieczorek-2"
<i>Proximate analysis</i>											
M ^{ad} , wt. %	6.6	7.8	12.5	3.9	12.4	4.7	10.9	2.6	0.9	4.2	2.6
A ^d , wt. %	21.0	15.5	10.9	8.1	11.9	21.1	9.9	17.1	24.8	16.7	3.0
VM ^{daf} , wt. %	56.59	57.06	55.86	59.14	39.56	39.10	38.21	37.82	34.04	37.68	33.94
<i>Elemental composition</i>											
C ^{ad} , wt. %	48.5	53.2	53.5	62.3	60.4	59.3	62.8	67.8	63.4	66.2	81.4
H ^{ad} , wt. %	3.79	3.93	3.93	5.48	3.46	3.83	3.70	4.14	3.77	4.16	4.59
N ^{ad} , wt. %	0.52	0.66	0.59	0.61	0.94	0.91	0.98	1.16	1.11	1.35	1.39
S ^{ad} , wt. %	1.41	1.52	0.63	1.02	1.22	1.09	1.08	0.48	0.88	1.34	0.34
S _A ^{ad} , wt. %	1.19	1.14	0.45	0.28	0.05	0.20	0.52	0.26	0.27	0.04	0.22
S _C ^{ad} , wt. %	0.22	0.38	0.18	0.74	1.17	0.89	0.56	0.22	0.61	1.30	0.12
O _{diff} ^{ad} , wt. %	20.77	19.73	19.71	19.17	11.23	10.27	9.15	7.38	6.28	6.79	7.55
Cl ^{ad} , wt. %	<0.005	0.022	0.013	0.009	0.131	0.399	0.164	0.320	0.202	0.026	0.293
<i>Heating values</i>											
HHV ^{ad} , kJ/kg	18,894	20,687	20,696	26,015	23,900	23,848	24,516	27,478	25,544	26,456	32,289
LHV ^{ad} , kJ/kg	17,905	19,639	19,533	24,723	22,842	22,897	23,442	26,511	24,699	25,445	31,223
<i>Chemical composition of ash (by ICP-OES)</i>											
SiO ₂ , wt. %	28.15	35.60	32.02	32.7	46.48	51.42	41.34	52.07	50.40	51.85	21.06
Al ₂ O ₃ , wt. %	21.60	9.49	12.63	24.5	28.42	27.03	33.50	21.77	25.99	32.87	16.96
Fe ₂ O ₃ , wt. %	6.04	12.00	2.58	11.4	9.59	7.23	10.88	9.00	7.27	5.26	10.07
CaO, wt. %	21.93	16.70	35.87	4.10	3.33	2.71	3.03	5.04	2.78	1.15	15.01
MgO, wt. %	4.36	1.75	1.12	6.24	2.76	3.30	1.90	4.48	2.66	1.27	8.72
P ₂ O ₅ , wt. %	0.63	0.11	0.06	0.18	0.15	0.13	0.12	0.34	0.58	0.63	0.35
SO ₃ , wt. %	15.21	21.30	11.89	10.0	1.46	2.61	1.51	3.25	2.29	0.59	19.72
Mn ₃ O ₄ , wt. %	0.04	0.10	0.05	0.10	0.03	0.13	0.03	0.27	0.07	0.03	0.24
TiO ₂ , wt. %	0.95	0.71	1.20	1.86	1.11	1.04	1.45	0.73	1.08	1.44	0.57
SrO, wt. %	0.09	0.11	0.35	0.02	0.06	0.05	0.05	0.08	0.07	0.10	0.18
Na ₂ O, wt. %	0.08	0.15	0.16	6.38	3.49	2.06	2.94	1.46	1.11	0.56	4.19
K ₂ O, wt. %	0.22	0.98	0.18	1.50	2.46	2.40	1.34	2.27	3.33	3.34	1.25
<i>Vitrinite/huminite reflectance</i>											
R, %	0.25	0.32	0.31	0.23	0.44	0.58	0.43	0.78	0.94	0.64	0.80

M – moisture content; VM – volatile matter content; A – ash content; HHV – high heating value, LHV – lower heating value, R – reflectance; ad – air-dried basis; db – dry basis; daf – dry and ash-free basis; diff – calculated by difference.

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