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# Temperature induced development of porous structure of bituminous coal chars at high pressure



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## ABSTRACT

The porous structure of chars affects their reactivity in gasification, having an impact on the course and product distribution of the process. The shape, size and connections between pores determine the mechanical properties of chars, as well as heat and mass transport in thermochemical processing. In the study the combined effects of temperature in the range of 973–1273 °K and elevated pressure of 3 MPa on the development of porous structure of bituminous coal chars were investigated. Relatively low heating rate and long residence time characteristic for the in-situ coal conversion were applied. The increase in the temperature to 1173 °K under pressurized conditions resulted in the enhancement of porous structure development reflected in the values of the specific surface area, total pore volume, micropore area and volume, as well as ratio of the micropore volume to the total pore volume. These effects were attributed to the enhanced vaporization and devolatilization, as well as swelling behavior along the increase of temperature and under high pressure, followed by a collapse of pores over certain temperature value. This proves the strong dependence of the porous structure of chars not only on the pyrolysis process conditions but also on the physical and chemical properties of the parent fuel.

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## 1. Introduction

The world economy is based on fossil fuel resources notwithstanding the emphasize given to the renewable energy systems and sustainable development. Gasification technologies have proven to be efficient and relatively clean methods of fossil fuels conversion into a product of versatile applications from heat and power generation to chemical synthesis and liquid fuels production (Bell, Towler, & Fan, 2011). In the recent years a renewed interest has been gained by underground coal gasification (UCG) in the context of technical or economic constraints related to the application of conventional coal extraction methods (Burton, Friedman, & Upadhye, 2006; Kostúr et al., 2015). Waste valorization (Mahinpey & Gomez, 2016; Smoliński & Howaniec, 2016) and biomass utilization in co-gasification (Howaniec & Smoliński, 2014a, b) is also of interest as well as the utilization of the excess or waste heat to increase the gasification process energy efficiency (Hori, Matsui, Tashimo, & Yasuda, 2005; Howaniec, Smoliński, & Cempa-Balewicz, 2015). The reactivity of a fuel chars in the process of gasification depends heavily not only on the parent fuel

properties but also on the operating parameters of the pyrolysis step (Griffin, Howard, & Peters, 1994; Howaniec & Smoliński, 2013). These parameters, including process temperature, pressure, heating rate and residence time, are known to be influencing the qualitative and quantitative characteristics of process products (Acevedo & Barriocanal, 2015; Cai et al., 1996; Fatemi, 1987; Griffin et al., 1994; Nassini, Fougá, Nassini, Bohé, 2016; Trubetskaya et al., 2016; Uguna, Carr, Snape, & Meredith, 2015), as well as swelling behavior and fluidity of a fuel (Lee, Jenkins, & Schobert, 1992; Lee, Scaroni, & Jenkins, 1991; Solomon & Fletcher, 1994). While the literature on the dependence between the process conditions and the products distribution is quite abundant, the knowledge on the relationships between the pyrolysis parameters and chars structure is not that comprehensive. The properties of porous structure of chars, including pore volume, area, pore size distribution, pore shape and pore network all define not only the physical properties of a material (density and strength) but also thermal conductivity and mass flow important in thermochemical processing (Rouquerol et al., 1994). The literature on the correlation between pyrolysis conditions and the development of porous structure of chars reported predominantly the effects of devolatilization temperature (Tremel, Haselsteiner, Nakonz, & Spliethoff, 2012; Yangsheng et al., 2010; Yu et al., 2007), fuel particle size (Xiumin et al., 2002; Yu

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et al., 2007) or fuel chemical pre-treatment (Fukuyama & Terai, 2008; Kopac & Toprak, 2007). In sparse studies pressure effects on porous structure of chars were considered and they were reported to be complex and dependent also on other parameters, i.e. coal rank, pyrolysis temperature, heating rate, and residence time (Khan & Jenkins, 1986; Lee et al., 1991; Wall et al., 2002). The effects observed in these studies are often contradictory: increase in pyrolysis pressure was claimed to decrease (Lee et al., 1992), but also to increase (Benfell et al., 2000; Tremel et al., 2012) the surface area of chars. The growth of the surface area with pressure followed by a subsequent decrease has also been reported (Howaniec, 2016a,b; Tremel et al., 2012). When high temperature is considered, as a single operating parameter influencing pore structure characteristics, it is in general reported to have a positive effect on the development of porous structure of chars reflected in the increased specific surface area and total pore volume (Yangsheng et al., 2010; Yu et al., 2007). Nevertheless, the decline in micropore volume or area, as well as in the specific surface area and the total pore volume with a rise in the process temperature over a certain boundary value has also been reported (Kopac & Toprak, 2007; Liu, Fang, & Wang, 2008; Yangsheng et al., 2010). This is primarily attributed to the initial intensive devolatilization and swelling with temperature rise, and subsequent collapse of a pore structure with further increase in the temperature (Kopac & Toprak, 2007; Yu, Xu, Yu, & Liu, 2005). These effects of a temperature-induced enhancement of porosity may be, however, diminished by pressure applied in pyrolysis (Tremel et al., 2012; Howaniec, 2016a,b). In the paper presented the effects of the pyrolysis temperature in the range of 973–1273 °K, under the pressure of 3 MPa, and with the application of relatively low heating rate and long residence time characteristic for the in-situ coal conversion on the development of porous structure of bituminous coal chars were examined. The study presented is considered to narrow the research gap on the influence of high pressure and temperature on the development of porous structure of chars. It may be also a useful contribution to the studies on sorption phenomena in the vicinity of georeactors.

## 2. Material and methods

### 2.1. Material

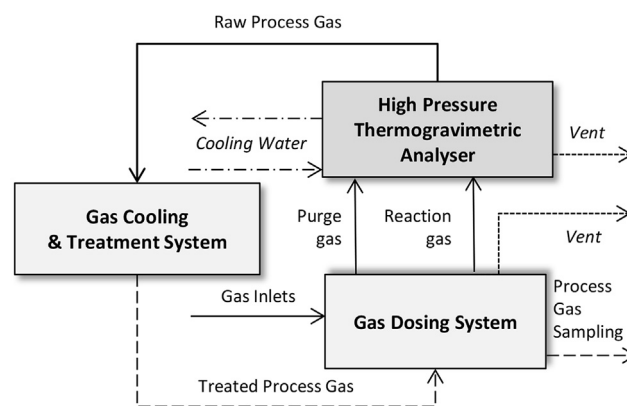
Bituminous coal was acquired, pre-treated and characterized in terms of proximate and ultimate analyses according to the relevant standards: PN-G-04560:1998 (moisture, ash and volatiles) with the application of automatic thermogravimetric analyzers LECO: TGA 701 and MAC 500; PN-81/G-04513, PN-ISO 1928:2002 (heat of combustion and calorific value) with the use of LECO calorimeters AC-600 and AC-350; PN-G-04584:2001 (sulfur content) employing an automatic analyzer TruSpec S by LECO; PN-G-04571:1998 (carbon, hydrogen and nitrogen contents) with the use of a TruSpecCHN analyzer; and PN-G-04516:1998 (oxygen and fixed carbon contents). The contents of macerals were quantified on the basis of PN-ISO 7404-3:2001 standard, and the vitrinite reflectance based on PN-ISO 7404-5:2002, with the use of polarization microscope Axio Imager D1. The results are shown in Table 1.

### 2.2. Methods

Pyrolysis tests were performed with the application of a high-pressure thermogravimetric analyzer (Rubotherm GmbH) with a magnetic suspension balance mechanism shown in Fig. 1. Coal samples of 1 g and particle size <200 µm were applied in the study. Samples were heated to the set process temperature of 973, 1073, 1173 or 1273 °K with the heating rate of 20 °K/min and pressurized to 3 MPa under argon. The residence time for chars at the set

**Table 1**  
Selected physical, chemical and petrographic data for coal tested.

No	Parameter, unit	Value	Measurement uncertainty, %
1	Moisture, %w/w	3.04	0.10
2	Ash, %w/w	4.21	0.05
3	Volatiles, %w/w	29.86	0.50
4	Heat of combustion, J/g	30,614	0.20
5	Calorific value, J/g	29,651	0.20
6	Total sulfur, %w/w	0.79	0.02
7	Combustible sulfur, %w/w	0.59	0.02
8	Carbon, %w/w	76.79	0.25
9	Hydrogen, %w/w	4.07	0.15
10	Nitrogen, %w/w	1.33	0.08
11	Oxygen, %w/w	9.97	0.50
12	Fixed carbon, %w/w	62.89	0.50
13	Vitrinite reflectance, %	0.65	0.01
14	Vitrinite, %vol.	35	3.00
15	Liptynite, %vol.	10	2.00
16	Inertinite, %vol.	55	3.00



**Fig. 1.** Schematic diagram of high pressure thermogravimetric analyzer.

process temperature was 5 h. The resulting chars, denoted as char 1–4, respectively, were next analyzed in terms of the porous structure properties.

Chars were ground and sieved to the fraction below 200 µm. The outgassing was performed overnight under vacuum at 393 °K. Next, the volumetric analysis was performed with the application of Autosorb iQ (Quantachrome Instruments, USA) equipped with a high vacuum system with a turbomolecular pump and low-pressure transducer. The nitrogen adsorption isotherms at 77 °K were determined as the basis for the characterization of chars in terms of the specific surface area (Brunauer-Emmett-Teller method, BET (Rouquerol et al., 1994)) and micropore area (V-t-deBoer method (de Boer, Linsen, van der Plas, & Zondervan, 1965)), the total pore volume (volume adsorbed at the relative pressure of 0.99) and the micropore volume (V-t-deBoer method), as well as pore size distribution (Density Functional Theory method, DFT (Rouquerol, Rouquerol, Sing, Llewellyn, & Maurin, 2014)).

## 3. Results and discussion

The measured parameters of the porous structure of chars developed under 3 MPa and at various temperature conditions are presented in Table 2.

The typical nitrogen isotherm determined at 77 °K for the chars tested shows the characteristic high volume adsorbed at low relative pressures, and narrow hysteresis loop, indicative of the presence of micro- and mesopores in the porous structure of chars (see Fig. 2).

**Table 2**

Parameters of porous structure of chars determined on the basis of nitrogen sorption isotherms at 77 °K.

Parameter, unit	Char 1 973 K	Char 2 1073 K	Char 3 113 K	Char 4 1273 K
Specific surface area, m <sup>2</sup> /g	19.1	108.4	190.0	101.1
Average pore diameter, nm	2.73	1.94	1.96	2.37
Total pore volume, cm <sup>3</sup> /g	0.013	0.053	0.093	0.060
t-method micropore volume, cm <sup>3</sup> /g	0.006	0.032	0.065	0.027
t-method micropore surface area, m <sup>2</sup> /g	16.2	85.4	164.9	68.3

The values of the average pore diameter determined on the basis of the nitrogen isotherms were in the range of small mesopores/large micropores (see Table 2). The largest average pore diameter was reported for chars produced at 973 °K, followed by the one for chars generated at the highest temperature tested. The average pore diameters of chars produced at 1073 and 1173 °K were similar and slightly lower than the values reported for chars 1 and 4.

The specific surface area and the total pore volume of chars produced under 3 MPa increased with the temperature of pyrolysis from 973 to 1173 °K, followed by a slight decrease at the maximum temperature tested of 1273 °K. The similar trend was observed in terms of the micropore area and volume (Fig. 3). The share of micropore volume in the total pore volume increased from 46 to 70% along the increase of temperature from 973 to 1173 °K and dropped to 45% at 1273 °K (see Table 2). The positive influence of temperature under atmospheric pressure on the porous structure development quantified with the use of the specific surface area and the total pore volume indicators for chars generated in the temperature range of 873–1073 °K was previously reported by Kopac and Toprak (2007). Further increase in the pyrolysis temperature to 1173 °K resulted in a slight decrease in the values of these parameters. This enhancement of porous structure growth under atmospheric pressure may be attributed to the intensive release of moisture, volatiles and swelling of coals along the increase of temperature. The subsequent drop in the pore surface area and volume with further temperature rise may be related to a collapse of pores resulting from breaking of cross-links in a carbon matrix over certain temperature (Kopac & Toprak, 2007). Increase in the total pore volume and micropore volume determined with

the application of mercury dilatometer with pyrolysis temperature rise from 293 to 873 °K was also reported by Yangsheng et al. (2010). The data was acquired for bituminous coal chars kept at the final process temperature for 5 h under pressure less conditions. The share of micropore volume in the total pore volume was, however, observed to decrease from approximately 19 to 3% with the temperature rise from 573 to 873 °K. These results vary from the ones reported in the study discussed and imply the significance of the combined effects of higher temperature and pressure on the porous structure development of chars. The increase in the share of micropore volume in the total pore volume with increase in pyrolysis temperature (from 1373 to 1673 °K) was previously observed by Yu et al. (2007) for bituminous coal chars prepared in a drop tube furnace in pressure less conditions. In the study presented the similar trend was observed in the temperature range of 973–1173 °K, but with a several times higher ratio of micropore volume to the total pore volume than the ones claimed previously (Yu et al., 2007) (see Table 2). This may imply the positive effect of pressure on the development of microporosity of coal chars at high temperature. This enhancement is, however, observed only to some limiting values of pressure and temperature over which a deterioration of the growth of porous structure is reported (Howaniec, 2016a,b; Tremel et al., 2012). Also swelling properties of a fuel, related to the content of volatiles, vitrinite and inertinite, as well as heating rate are considered to be affecting porosity of chars (Benfell et al., 2000; Solomon & Fletcher, 1994; Yu et al., 2007). The intensity of swelling was reported to be dependent on volatiles content and process temperature with the highest intensity observed for coal of volatiles content of 25–28% (Khan & Jenkins, 1986) and process temperature of 1573 °K (Yu et al., 2007). The enhancement of swelling, contributing to the development of porous structure of chars along the increase of pressure was observed (Lee et al., 1991), as well as the limiting value of pressure over which a decline in swelling was reported (Lee et al., 1991; Solomon & Fletcher, 1994; Wu, Bryant, Benfell, & Wall, 2000). This is in line with the observations made within the study presented where coal of relatively high inertinite and vitrinite content and volatiles concentration of 30%vol. gave chars of increasing porous structure development along the increase of temperature followed by a decrease in specific surface area, total pore volume and micropore volume and area with further rise in temperature under high pressure conditions.

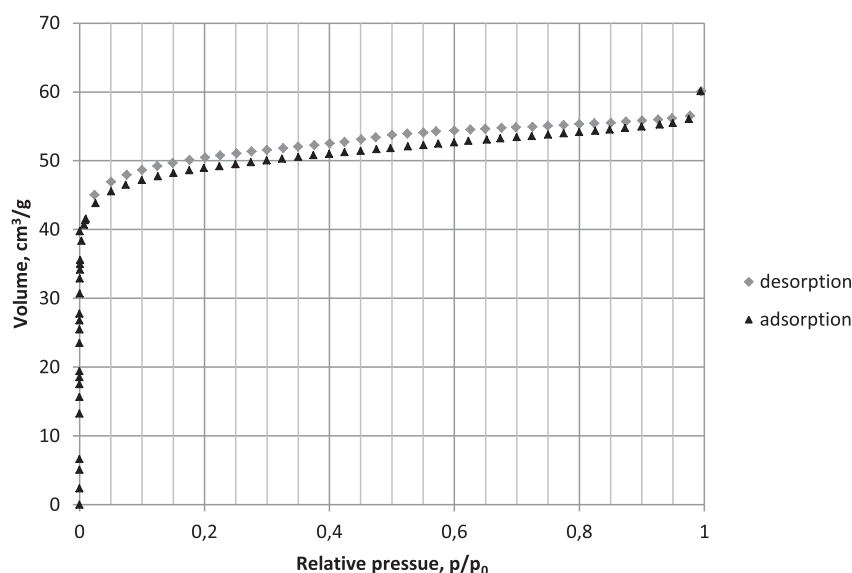


Fig. 2. Exemplary nitrogen sorption isotherm at 77 °K for Char 3 (1173 °K, 3 MPa).

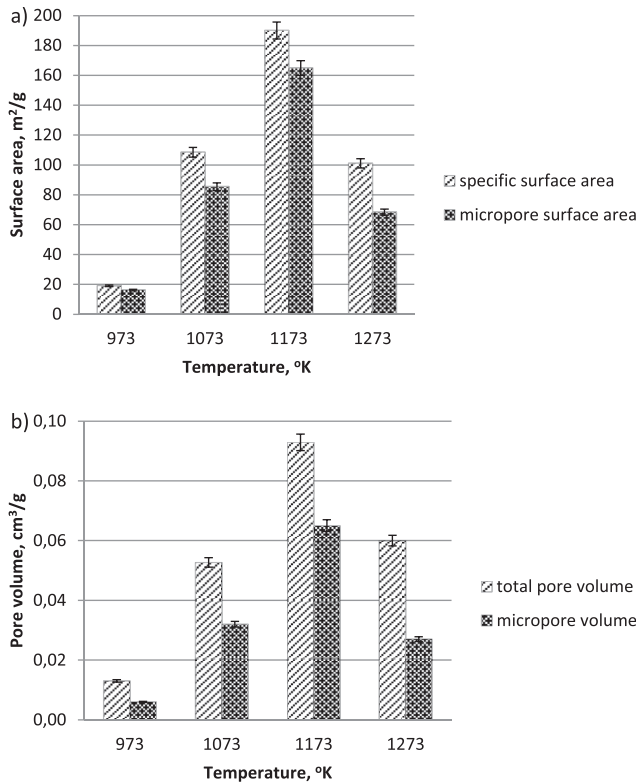


Fig. 3. The effect of temperature applied in coal pyrolysis at 3 MPa on a) pore surface area and b) pore volume of chars on the basis of nitrogen sorption isotherms at 77 °K.

The indication of the opposite trend, i.e. a decrease in micropore surface area of bituminous coal chars prepared in a drop tube reactor under atmospheric pressure with the temperature rise from 1173 to 1673 °K was reported by Liu et al. (2008) on the basis of carbon dioxide adsorption isotherm at 273 °K, which is relevant to pores of a diameter below 1.5 nm. However, no data on micropore volume change with temperature was given in this study. Tremel et al. (2012) also reported a decrease in a surface area determined on the basis of carbon dioxide sorption isotherms for chars prepared both under 0.5 and 2.5 MPa with the increase in temperature from 1473 to 1673 °K and in residence time. This study was, however, performed for lignite chars produced in an entrained flow gasifier with residence times significantly lower than the ones applied in the study presented (below 3 s). Such effects may be related to the suppression of vaporization and volatiles yield with increasing pressure, notwithstanding the positive effects of temperature on the release of moisture and volatiles (Wall et al., 2002). The results reported here are in line with some previous observations, though the opposite trends are also claimed in the literature. This is because the literature in the field concerned is sparse and the subject of the studies is often limited to analyzing one parameter as a variable (predominantly the pyrolysis temperature). This implies the need for further studies in the area in the context of the impact of porous structure of chars on the heat and mass transport, and the resulting effects of thermochemical processing.

#### 4. Conclusions

Based on the observations of the study presented it may be concluded that the increase in pyrolysis temperature from 973 to 1173 °K under elevated pressure of 3 MPa results in the enhanced development of bituminous coal chars porous structure followed

by a slight deterioration of its properties at the maximum temperature tested of 1273 °K. This trend is reflected in the values of the specific surface area, total pore volume, micropore area and volume as well as share of micropore volume in the total pore volume. The ratio of micropore volume to the total pore volume is high, in general increases with temperature and amounts to 45–70%. These results may be attributed to the combined effects of the enhanced vaporization and devolatilization at high temperatures, intensified swelling behavior with the rise in temperature, and subsequent collapse of porous structure over certain temperature in pressurized conditions. They are also expected to be strongly dependent on a parent fuel properties, such as moisture and volatiles content, as well as concentration of vitrinite and inertinite.

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