



## Research article

# Development of porous structure of lignite chars at high pressure and temperature



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## ABSTRACT

Lignite comprises a considerable element of the world energy balance resources applicable for thermochemical conversion with conventional methods of combustion or gasification, but also with the unconventional techniques of the in-situ processing for energy recovery. The porous structure of chars affects the thermal conductivity, as well as flow and sorption phenomena, which are key factors in thermochemical processing of fossil fuels. Yet, the literature data on the temperature, and especially pressure induced development of the porous structure of lignite chars is extremely limited. In the study the characteristics of lignite chars produced under 1, 2, 3, and 4 MPa and at 1273 K was presented. The enhanced porous structure development with pressure increase, followed by a slight reduction in surface area and pore volume with further pressure rise was observed. The pressure conditions of the peak development of porous structure differed for various lignite samples tested. The importance of devolatilisation for microporosity growth and moisture release for the development of the total porous structure under the process conditions applied were also indicated. The results proved the complex effect of the specific process conditions applied in the study, and fuel characteristics on the growth of porosity of lignite chars.

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## 1. Introduction

Lignite and sub-bituminous coal represent approximately 55% of the world coal reserves [1]. In Poland, over 40% of electricity generation is based on lignite making it an important element of energy resources [2]. For countries with the energy security heavily dependent on fossil fuels, the wide implementation of highly efficient, and environment friendly solid fuel conversion technologies, like pyrolysis or gasification, is a necessity. Gasification technologies have been continuously developed for several decades now, since they offer relatively clean, gaseous product with versatile application possibilities [3]. Recently, there has been also a renewed interest in underground coal gasification (UCG), especially applicable for coal deposits unmineable with conventional techniques for technical or economic reasons [4,5]. Lignite is claimed to be in particularly suitable for UCG for its high permeability when compared to higher rank coals [6–8]. The pyrolysis, on the other hand, may be considered as the process of thermochemical conversion of carbonaceous material in itself, or as the inevitable, initial step of chars formation in combustion or gasification systems. Therefore, the operating parameters of the pyrolysis not only determine the amount and quality of its liquid and gaseous products, but also define the properties of the resulting chars, including their reactivity in the subsequent gasification. In turn, the transformations of a fuel during pyrolysis determine the efficiency and the course of the gasification process. Here, the porous

structure of chars, being the resultant of chemical and physical characteristics of a carbonaceous material, but also of the specific pyrolysis conditions applied (i.e. heating rates, peak temperature and process pressure) is of major significance. The volume, area, shape and interconnections between the pores are known to delimit density and mechanical strength of materials, but more importantly, they also affect the thermal conductivity, as well as flow and sorption phenomena, which are key factors in thermochemical processing of fossil fuels [9,10].

Vast amount of literature has been devoted to the effects of pyrolysis conditions on the process efficiency, type and yields of products, as well as the reactivity of the resulting chars in gasification [3,11,12]. In some studies, the influence of temperature, fuel particle dimensions and physical or chemical treatment of carbonaceous materials (predominantly bituminous coal and biowaste) on porous structure of chars or, so called, activated carbons was reported [13–22]. The pyrolysis pressure is claimed to have some effect on devolatilisation and plastic properties of bituminous coal at elevated temperatures [13–15], but the influence of pressure on the development of porous structure of chars is still poorly recognized [13,15–19]. This lack of data is, to some extent, understandable when the complexity of the combined effects of various factors on the characteristics of porous structure is considered; to mention only fuel composition, heating rates, residence times and pyrolysis temperature applied [13,17,18]. This limited and often contradictory data on the development of porous structure of chars is even more scarce when lignite as chars precursor is considered [6,23–30], and practically missing when the external pressure effects on porosity of

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**Table 1**  
Chemical and physical characteristics of lignite samples.

No	Parameter, unit	L1	L2	L3	Uncertainty
1	Moisture W, %w/w	7.18	12.97	14.24	0.10%
2	Ash A, %w/w	9.12	23.07	12.63	0.10%
3	Volatiles V, %w/w	47.18	37.53	36.90	0.50%
4	Fixed carbon, %w/w	36.52	26.43	36.23	0.50%
5	Sulfur S, %w/w	1.32	2.84	1.78	0.05%
6	Carbon C, %w/w	56.82	42.63	51.03	0.25%
7	Hydrogen H, %w/w	5.00	3.21	3.65	0.15%
8	Nitrogen N, %w/w	0.54	0.34	0.83	0.08%
9	Oxygen O, %w/w	20.22	15.37	16.11	0.50%
10	Heat of combustion $Q_d$ , kJ/kg	23,942	16,602	19,640	0.30%
11	Calorific value $Q_i$ , kJ/kg	22,675	15,585	18,405	0.30%

this type of chars are concerned. This is a serious research gap since the system of pores, their size, shape and interconnections, all affect the heat and mass transport properties, and in turn, may provide a valuable insight into the observed specific effects of thermochemical conversion of solid fuels and fuel blends [30–33], other applications of devolatilized carbonaceous materials [23–27], as well as the environmental aspects of the post-UCG process sorption [34]. There is a clear need for studies on pressure effects on lignite chars development, bringing new insights into the chars performance in pressurized gasifiers, and potential for UCG process by-products sorption in a post-gasification cavity.

In the paper the results of the study on the effects of pyrolysis pressure of 1, 2, 3 and 4 MPa on the development of porous structure of lignite chars are presented. The chars tested were prepared at relatively low heating rate, high temperature (1273 K), and long residence time at the final temperature more applicable in the description of the UCG process than the values typically employed in the research presented in the literature. Chars precursors differed in terms of physical and chemical characteristics and were sampled from various lignite deposits. The micro- and mesoporosity was determined with the application of nitrogen sorption isotherm data at 77 K, and methods enabling the qualitative and quantitative characterization of wide range of meso- and micropores in a single measurement. The work presented is considered to be contributing to the limited and desirable research on characterization of pressure-induced porous structure development of chars. Such data is clearly missing from the literature in case of lignite as chars precursor. The results are the starting point for gas sorption studies on solid residuals of lignite underground coal gasification, simulating the post-process sorption of various gaseous constituents in the vicinity of the georeactor. As such, they are expected also to complement the studies available in the literature on sorption of various hydrocarbons on raw coals [35,36]. All the above mentioned aspects, including the research objective, the fuel type, and the experimental conditions applied contribute to the novelty of the research presented and to the potential of its results for future studies.

## 2. Experimental

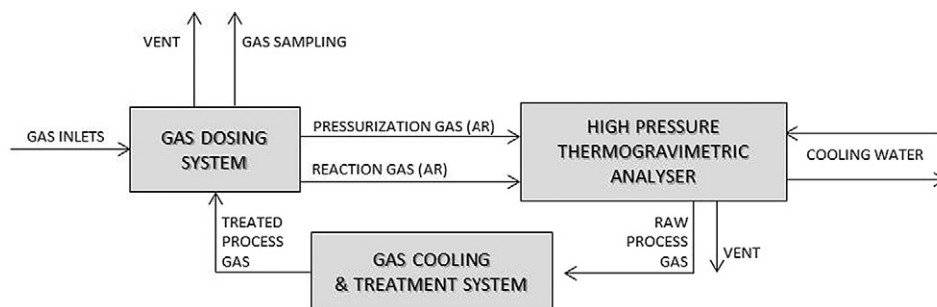
### 2.1. Samples

Fuel samples provided from lignite deposits Turów, Bełchatów (Szczerców) and Sieniawa, denoted as L1, L2 and L3, respectively, were ground and sieved to the fraction below 200  $\mu\text{m}$ . Next their characterization in analytical state (PN-G-04502:2014-11) in terms of moisture, ash and volatiles content (PN-G-04560:1998, using automatic thermogravimetric analysers LECO: TGA 701 and MAC 500), heat of combustion and calorific value (PN-G-04513:1981 with the application of LECO calorimeters: AC-600 and AC-350), sulfur content (PN-G-04584:2001 using an automatic analyzer TruSpec S by LECO), as well as carbon, hydrogen, and nitrogen contents (PN-G-04571:1998 with the use of a TruSpecCHN analyzer) was performed. Oxygen and fixed carbon contents were calculated by difference (PN-G-04516:1998). The respective data is given in Table 1.

Lignite samples were processed in the inert gas atmosphere (argon) in a high pressure thermogravimetric analyzer with a magnetic suspension balance mechanism (Rubotherm GmbH) to produce chars under various pressure conditions of 1, 2, 3 and 4 MPa. The uniqueness of the analyzer results from the capability of thermogravimetric measurements to be performed under high pressure, and also on samples significantly larger than applicable in conventional TGA instruments. It is equipped with automatic control and indicating system, including automatic gas dosing, data acquisition and recording. The resulting chars were denoted as e.g. L1–4, with the second figure indicating the pressure applied in pyrolysis. The schematic diagram of the installation is presented in Fig. 1. A sample of 1 g and particle size below 200  $\mu\text{m}$  was put into the crucible, pressurized to the pre-set value, heated with the heating rate of 20 K/min to 1273 K, and processed under the final pressure and temperature conditions for 5 h.

### 2.2. Porous structure characteristics

Chars were sieved to the fraction below 200  $\mu\text{m}$  (PN-ISO 3310-1:2000) and degassed under vacuum and at the temperature of 393 K overnight [9]. The porous structure characterization was performed with the application of the Autosorb iQ analyzer (Quantachrome Instruments, USA) equipped with a high vacuum system with a turbomolecular pump and low-pressure transducer. The determination of the specific surface area was based on the nitrogen sorption isotherm at 77 K and the multipoint Brunauer-Emmett-Teller (BET) method [37]. The micropore and mesopore structure was examined using nitrogen sorption data at 77 K, the Density Functional Theory (DFT) method for pore size distribution, and the V-t-deBoer method for micropore volume and surface area quantification [38,39]. The total pore volume was determined as the volume adsorbed at the relative pressure of 0.99. The configuration of the analyzer and the methods applied enabled qualitative and



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

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