



Sorption of CO₂ on low-rank coal: Study of influence of various drying methods on microporous characteristics



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ABSTRACT

Various drying procedures were applied to North Bohemian low-rank coal. Dried samples were subjected to CO₂ sorption analysis. Adsorption data were evaluated according to the Dubinin–Radushkevich and Medek equation to describe the micropore parameters. It was proven that drying conditions may have an impact on the monitored characteristics of the studied coal, particularly on the surface area of the micropores and the abundance of the most frequent pores. The observed textural parameters do not depend on the drying period but are a function of the drying temperature and may also be influenced by the presence of an oxidising atmosphere. Temperatures higher than 60 °C can cause alterations in the structure of the coal. Both the surface area of the micropores and the abundance of the most frequent pores of the studied coal increase in the following range of techniques: convection oven drying < inert-gas purging, microwave irradiation < hot-oven vacuum pumping < freeze-drying (lyophilisation). Due to the specific drying conditions, the freeze-dried sample showed the highest surface area of micropores.

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1. Introduction

Low-rank coal is an important natural material used, in addition to electricity generation, in many other technological applications (e.g., Bromhal et al., 2005; Busch and Gensterblum, 2011; Ruth, 1998). Nevertheless, its high moisture content may play an undesirable role (Aziz et al., 2012; Day et al., 2008; Karthikeyan et al., 2009; Osman et al., 2011; Švábová et al., 2012; Yu et al., 2013). For that reason, subjecting low-rank coal to a drying process is often necessary even though this can result in the destruction of its gel-like structure (Androutopoulos and Linardos, 1986; Deevi and Suuberg, 1987; Ozdemir and Schroeder, 2009; Suuberg et al., 1993; Yu et al., 2013). Greater attention has not been paid to this process due to the variability of drying methods.

This paper examines the effects of various drying conditions on the microporous textural characteristics of low-rank coal observed by CO₂ adsorption. The influences of the drying period, drying temperature as well as the oxidising/inert atmosphere were investigated by hot-oven

drying under and without vacuum, purging of the sample with an inert gas, freeze-drying (lyophilisation) and by microwave irradiation.

2. Experimental

2.1. Samples

A sample of subbituminous coal taken from the Czech part of the North Bohemian Coal Basin (denoted as HR) was chosen for the main purpose of this study. In addition, a sample of another subbituminous coal of North Bohemia (denoted as V) and German lignite (denoted as M) was examined to verify changes in their structure induced by deep freezing (Section 3.4). Table 1 summarises the basic characteristics of the coal samples.

The samples were crushed in a ball mill to obtain a grain size of 0.06–0.15 mm. Oversized fractions were repeatedly returned to the mill.

2.2. Drying methods

The five following drying procedures were applied to the coal sample with regard to studying their impact on its microporous textural parameters. The repression of oxidation processes during drying should occur in the case of methods #1, #2 and #3, whereas possible oxidation of coal is expected in procedures #4 and #5. The medium vacuum used

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Table 1
Analyses of the samples.

Sample	Moisture (wt.%, as received)	Ash (%, db)	C (%, db)	H (%, db)	N (%, db)	S ^{tot} (%, db)	O ^{diff} (%, db)
HR	17.5	8.0	68.4	6.0	0.9	1.2	15.5
V	17.0	22.7	55.6	4.9	0.7	1.0	15.1
M	40.0	10.9	59.5	4.8	0.8	1.8	22.2

db – dry basis, tot – total, dif – by difference.

during experiments #1 and #3 was provided by an oil pump. For the drying experiments, about 2 g of coal were used. The effort was to obtain a dry sample time-effectively and with maximum restoration of its microporous texture.

- (#1) Hot-oven vacuum drying. The influence of both the drying period and temperature was studied in this method. The sample was placed on an aluminium dish, forming a ca. 1 mm thickness on its bottom. The effect of the drying period was investigated at 2, 5 and 8 h at a constant temperature of 60 °C. The effect of the drying temperature was examined at 60, 70, 80 and 105 °C for a constant drying period of 2 h.
- (#2) Inert-gas purging of the sample with a nitrogen atmosphere (99.995% of purity) was carried out at 60 and 105 °C for 2 and 5 h. The sample was placed on the bottom of a glass U-tube during the purging procedure.
- (#3) Freeze-drying (lyophilisation). Before the procedure, the sample was flooded with liquid nitrogen (–196 °C). The actual sample temperature during the lyophilisation procedure was not monitored, however, the temperature in the condenser chamber was kept at –87 °C. This drying procedure lasted for 5 h.
- (#4) Convection oven pre-treatment was performed at 60 °C for 5 h. The coal sample was placed on an aluminium dish, forming a ca. 1 mm thickness on its bottom.
- (#5) Microwave irradiation. The sample was placed in the centre of a microwave oven in a glass weighing bottle that was stationary during the drying, which lasted for 20 min at power output 320 W. A programmable Sencor SMW5020 microwave oven with a maximum power output of 800 W and frequency 2.45 GHz was used.

All of the above methods provide samples below 0.3 wt.% of residual moisture, which we consider to be dry. The exceptions are the samples treated at 60 °C by techniques #2 and #4 which exhibited residual moisture of 1.4 and 0.9 wt.%, respectively. Nevertheless, these samples are kept in this study due to their interesting behaviour.

In the original scope, the above methods were extended by purging of a coal sample in pure oxygen (as in procedure #2) to determine the effect of an oxidising atmosphere. Unfortunately, this procedure as well as long-term ambient desiccator drying was excluded from this study due to the high residual moisture content of the resulting samples ($W_{res} > 2$ wt.%). The high content of residual water can be associated with an oxidation atmosphere which promotes the formation of water as a product of low-temperature oxidation of coal (e.g., Wang et al., 2002a, 2002b).

The quantitative analysis of the residual moisture content was performed under a convection aerial atmosphere at 105 °C until constant mass change according to the ČSN 441377 standard.

2.3. CO₂ sorption measurements

Dried samples were subjected to CO₂ (99.995% of purity) adsorption analysis by means of a Setaram PCTPro E&E volumetric analyser. The weight of the sample was approximately 0.7–0.8 g. All the measurements were carried out at 30 °C over a relative pressure range from 0 to 0.014 p_{eq}/p_s (i.e., 0–1 bar of absolute pressure expression) where p_{eq} and p_s are the equilibrium and saturated CO₂ pressures, respectively.

The CO₂ pressure was increased stepwise ($\Delta p = 0.15$ bar) and if the rate constant of adsorption dropped below $1 \cdot 10^{-6}$ wt.% min⁻¹ after ~40 min, a further CO₂ dose was admitted to the sample. Usually, 10-point adsorption isotherms were obtained. The dead volume of the sample cell was measured by the helium (99.996% of purity) expansion technique. Hy-Data E&E software (Setaram) was used to specify the different adsorption parameters.

2.4. Evaluation of the adsorption isotherm data

The Dubinin–Radushkevich (D–R) isotherm was used to fit the adsorption equilibrium data of carbon dioxide. The D–R model assumes Gaussian distribution of the adsorption potential and is described by the following equation (Gregg and Sing, 1982):

$$\ln V = \ln V_{mi} - \left(\frac{RT}{E}\right)^2 \ln^2 \left(\frac{p_s}{p_{eq}}\right) \quad (1)$$

where V is the volume of micropores occupied by adsorbed CO₂ at equilibrium pressure p_{eq} , V_{mi} is the limiting (total) volume of micropores, R is the gas constant, and p_s term is the saturated pressure of CO₂ vapour at temperature T ($p_s = 72.76$ bar). E is the characteristic energy of CO₂ corresponding to the net heat of adsorption (e.g., Day et al., 2008; Švábová et al., 2012). The D–R equation manifests a linear plot in coordinates $\ln V$ versus $\ln^2(p_s/p_{eq})$. From the $\ln V_{mi}$ intercept of the plot, the limiting value of the micropore volume V_{mi} was evaluated. The molar density of the adsorbed (liquid) phase of CO₂ was taken as 73.59 cm³ mol⁻¹.

To evaluate the surface area of the micropores S_{mi} , the Medek equation was applied (Medek, 1977) which for the Gaussian distribution can be written in the following form:

$$S_{mi} = 2 \cdot V_{mi} \cdot \left(\frac{E}{k}\right)^{\frac{1}{3}} \cdot \Gamma\left(\frac{7}{6}\right) \quad (2)$$

where k is the constant characterising the interactions between the CO₂ and carbonaceous surface ($k = 3.145$ kJ nm³ mol⁻¹, Medek, 1977; Prinz and Littke, 2005), and Γ stands for the gamma function (value of $\Gamma(7/6) = 0.928$).

In addition to surface area S_{mi} , Medek also refers to the possibility to evaluate the distribution curve of the micropores (Medek, 1977). For the Gaussian distribution of the adsorption potential, the equation takes the form:

$$\frac{dV}{dr} = 6 \cdot V_{mi} \cdot \left(\frac{k}{E}\right)^2 \cdot r^{-7} \cdot e^{-\left(\frac{k}{E}\right)^2 \cdot r^{-6}} \quad (3)$$

where r is the equivalent radius of the micropore. Based on Eq. (3), the mode (i.e. most common) equivalent micropore radius r_{mode} could be calculated. However, in the present study, all the values of r_{mode} were either 0.66 or 0.67 nm, thus practically confirming the independency of the drying procedure of the sample. On the other hand, the abundance of the most frequent pores (dV/dr)_{mode} proved sensitivity to the pre-treatment procedure of the sample. Thus, the frequency of the most common (micro)pores (dV/dr)_{mode} was evaluated from Eq. (3) and is further discussed as a parameter related to sample drying method.

To determine possible errors in all the experimental procedures (including both pre-treatment and the adsorption process), seven HR samples were taken and dried at 60 °C for 2 h as described in method #1 and then subjected to CO₂ sorption measurement. The following mean values of the seven replicates \pm standard deviations were obtained: $S_{mi} = 278 \pm 4$ m² g⁻¹, $E = 9.79 \pm 0.11$ kJ mol⁻¹ and $(dV/dr)_{mode} = 0.330 \pm 0.005$ cm³ g⁻¹ nm⁻¹. This corresponds to relative standard deviations of about 1.5% for each parameter.

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