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High pressure desorption equilibrium of lignite obtained by the novel isochoric method

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HIGHLIGHTS

- ▶ A novel isochoric method of measuring desorption equilibrium was developed.
- ▶ Desorption equilibrium of lignite at high pressures and temperatures was measured.
- ▶ The BET equilibrium equation was fitted to the data points with improved R^2.

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ABSTRACT

The most promising method of coal drying is the high pressure superheated steam drying (HPSHSD). High temperature and pressure sorptional equilibrium of lignite used in HPSHSD design is rarely available. The measurement requires either complex equipment or is time and labor consuming. In this work a novel isochoric method of high temperature and pressure desorption equilibrium measurement is described which uses a standard autoclave and easy to follow experimental procedure. Using this method the desorption equilibrium of low rank coal of Bełchatów open pit mine was measured in the range of temperatures up to 200 °C and pressures up to 23.6 bar. A BET type equation was fitted to the experimental data with correlation coefficient of 0.960. The results obtained compare well to the results obtained for low rank coal using much more sophisticated equipment.

1. Introduction

The energy needs of mankind are immense and grow constantly. The most of the energy produced comes from fossil fuels: coal, crude oil and gas. Of these only low rank coal deposits are expected to last longer than 50–100 years. It is the resource, which now offers the highest energetic safety to Poland and the rest of the world [1,2]. The world's available deposits of low rank coal are estimated as 512 billion Mg (512×10^9 tons), which would steadily provide for energetic needs of mankind in a time perspective of at least 300 years [1,2]. At the same time low rank coal is competitive in price per unit of energy with other fuels [3,4]. In Poland low rank coal deposits are estimated as 2.1 billion tons, of which Bełchatów open pit mine excavates 38 million tons per year.

Unfortunately the low rank coal contains 30–70% (w.b.) moisture when excavated [5,7]. When ineffectively dried in a boiler system a waste of energy carried away with combustion gases is inevitable. Much better solution is a pre-drying of coal before combustion in highly energy efficient superheated steam drying system [5–17]. The emanating steam can be reheated and re-circulated, which allows for elimination of atmospheric pollution [18]. The excess steam can be condensed and its energy recovered. A promising variety of superheated steam drying (SSD) is HPSD which has higher energy efficiency than ordinary SSD [19].

Besides of providing much higher energy efficiency than traditional drying, SSD also eliminates a risk of oxidation and ignition due to the use of oxygen-free atmosphere. It was also found that steam dried coal is less prone to self-ignition [6,9,20] and thus good for storage.

One of the important thermodynamic properties essential in the design of coal drying, either in air or in steam, is the sorptional equilibrium i.e. the relationship of coal moisture content on the relative pressure of water vapor in the surrounding atmosphere.

2. Earlier work

Low rank coal is a porous and hygroscopic material. Water in coal exists not only on its macroscopic surface but also inside particle and is bound to it by absorption, adhesion and capillary forces [6,21,22]. When exposed to gaseous medium, either air or superheated steam, on the surface of the solid a thermodynamic

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Nomenclature

a_1, a_2, a_3	BET T equation coefficients
B	second virial coefficient (m^3/kmol)
C	third virial coefficient ($m^6/kmol^2$)
m	mass (kg)
m_e	mass of water in sample at equilibrium (kg)
m_L	initial mass of water in sample (kg)
m_p	initial mass of sample (kg)
m_S	sample dry mass (kg)
M	molar mass (kg/kmol)
P	total pressure (kPa)
P_c	critical pressure (kPa)
p	partial pressure (kPa)
p_s	saturated water vapor pressure (kPa)
p_{in}	initial pressure (kPa)
p_e	equilibrium pressure (kPa)
R	universal gas constant (kJ/kmol K)
T	temperature (K)
T_c	critical temperature (K)
T_r	reduced temperature
t_{in}	initial temperature (°C)
t_e	equilibrium temperature (°C)
V	molar volume (m^3/mol)
V_a	autoclave volume (m^3)
V_c	critical molar volume (m^3/kmol)
V_p	sample volume (m^3)
X_e	equilibrium moisture content (kg H_2O/kg)
y	molar fraction (–)
ρ	gas phase density (kg/m^3)
ϕ	relative pressure (–)
ω	acentric factor

Subscripts

1	water vapor
2	nitrogen
3	carbon dioxide
m	mixture

equilibrium is quickly established. The knowledge of the equilibrium value of material moisture content X_e and corresponding degree of saturation of water vapor (relative pressure) ϕ is essential for establishing boundary conditions in the formulation of equations for water transport during solving drying problems of coal by the, so called, diffusion models or shrinking core models [8].

The relation of the relative pressure on the moisture content at constant temperature is called a sorption isotherm. The relationship can be measured either for water uptake or release which correspond to wetting or drying, respectively. Since sorption hysteresis can occur i.e. both curves are usually not identical, sorption isotherms must be identified as adsorption or desorption isotherms. Sorption isotherms form a 3D surface in X, T, ϕ coordinate system. It is essentially unimportant if the equilibrium was obtained at constant temperature, constant pressure or constant volume of the system. Corresponding curves are called sorption isotherms, isobars and isochors. It is also unimportant whether water vapor in the gas phase exists alone or in mixture with gases, provided that the other gases are inert i.e. do not adsorb nor condense on the solid surface. In the first case the water vapor pressure is the total pressure, in the other it is a partial pressure.

The simplest and the most frequently used method of measuring sorption isotherms by weighing the solid sample in the atmosphere of ϕ controlled by saturated solutions of selected salts is the desiccator method [23–26] or the vacuum microbalance method [26]. In the desiccator method measuring each point requires a new sample and the equilibrium sets very slowly. The vacuum microbalance method uses only one sample and is much faster. The automated microbalance method – DVS allows for easy and rapid sorption isotherm measurement [23,26].

Low temperature sorption isotherms of low rank coal are widely available in literature. The earliest noted measurements of adsorption and desorption isotherms at 20 °C [25] as well as 20 °C and 40 °C [24] were made for low rank coal of North Dakota. Much later Allardice and Evans [27] investigated adsorption and desorption isotherms of brown coal excavated in Yallourn open-pit mine in Australia. They were investigated at 30 °C, 40 °C, 49 °C and 60 °C. Toei and Tamon [28] investigated sorption isotherms of brown coal from Morwell, Australia at 5 °C, 20 °C and 30 °C. Fei et al. [26] compared sorption isotherms of Victorian lignites at 30 °C obtained by three different methods of measurement. Sorption isotherms for chemically treated coals were presented by Allardice et al. [23] at 30 °C for 15 raw samples, four acid-washed samples and seven hydrothermally dewatered samples, and Fei et al. [29] for coals after removal of soluble inorganic salts and cations.

In our earlier work [30] desorption isotherms of brown coal from open-pit mine of Bełchatów, Poland were measured using desiccator method at 25 °C, 30 °C, 40 °C, 50 °C, 60 °C, 70 °C, 120 °C and under atmospheric pressure.

In general the observed desorption isotherms exhibit an S-shaped form classified as type II of the Brunauer et al. [31] classification. The lower segment corresponds to monolayer adsorption, the middle segment to multilayer adsorption and the upper segment is due to capillary condensation. The equilibrium moisture content decreases when temperature is increased at the same relative pressure of water.

It is clear that desorption isotherms measured at temperatures below saturation temperature of water vapor are only suitable for air drying, where solid temperatures are low. In superheated steam drying temperatures exceed saturation point temperature, which depends on the working pressure and the degree of superheat. Desorption equilibrium in superheated steam is usually presented in the form of a sorption isobar, which represents the dependence of equilibrium moisture content on steam temperature at given pressure. In the earlier work [30] a desorption isobar of Bełchatów lignite was measured at atmospheric pressure at the following points: 120 °C, 140 °C, 160 °C, 180 °C, 200 °C. The equilibrium moisture content was measured by weighing the sample hanging in the steam chamber with an external balance connected to the sample by a thin wire passing through a small hole in the chamber. When the internal chamber pressure is close to the atmospheric only small acceptable outflow of steam is observed through the wire hole. At high pressure this construction would lead to excess flow of steam and therefore it has been modified by many researchers as shown in Fig. 1.

The balance chamber is purged by cold helium or nitrogen gas stream providing cooling of the balance. Pressure in the balance chamber is slightly higher than that of the steam chamber thus steam cannot penetrate into the balance chamber and condense there. Because inert gas infiltrates the steam chamber it must be removed together with excess steam. Thus a constant steam flow