Full Length Article

Multi-component gas mixture transport through porous structure of coal

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ABSTRACT

A study of gas flow through porous coals is significantly important for the accurate assessment of the state of endogenous fire risk. Coal characterizes of a unique pore structure which provides a good storage capacity and an ideal transport pathway for the movement of gases. Gaseous products released from the source of coal self-heating flow through coal and may be subject to adsorption. In this study, the effects of the transport of multi-component gas mixture through a sorption column filled with granular coal and inert material were investigated. The experiment with coal presented in the paper proved that gas concentrations at the inlet (Co) and at the outlet of the sorption column (Ck) varied depending on the properties of coal and gas molecules. Based on the results, an index demonstrating the relationship between these concentrations was calculated. The experiment of gas mixture flow through inert material confirmed that the lowest index, i.e. below 0.7, obtained for propylene and acetylene in the experiment with coal was a result of sorption processes. Gases with lowest critical temperatures, such as carbon monoxide and hydrogen had the highest index which was above 0.9.

1. Introduction

As a source of serious losses resulting from a temporary isolation of mining areas, endogenous fire is a negative phenomenon and it is also a risk for the work safety. In the case of mines with methane hazard, the fire may additionally cause the ignition and explosion of methane. Generally, it is a naturally occurring process caused by coal ability to self-heating under given conditions. It takes place when the heat emitted from the exothermic reaction of coal with oxygen from the air is accumulated. The tendency of coal to self-heating is a function of a number of controllable and uncontrollable factors which can be divided into internal and external ones. The internal factors are associated with the physical-chemical parameters of coal whereas the external ones are related to the climatic conditions underground, the method of mine ventilation and coal extraction. The detection of spontaneous combustion in its early stage is very important for its prevention; in addition, it makes it easier to deal with it. The process may be detected by physical symptoms by means of the human senses (characteristic odor, formation of water droops on cooler surfaces), thermal devices or chemical methods. The chemical method is commonly used in the world and it is based on monitoring gas concentrations in mine air and on analyzing their changes [1,2]. During a low-temperature coal oxidation process different gases such as CO, CO_2, H_2 as well as hydrocarbons are emitted [3]. The composition of gas mixture changes with coal temperature. As the temperature of coal increases exponentially, the concentration of

carbon monoxide and hydrogen as well as the production of hydrocarbons such as: ethylene, propylene, acetylene increase significantly but the oxygen concentration simultaneously decreases. Based on the amount and the trend of changes in gas concentrations in time, the development of the coal self-heating process is assessed. However, the concentration of gases determined in measuring stations for the early detection of endogenous fires may be lower than the concentration in the source of fire due to the dilution of ventilation air or because the gases are trapped in coal, which consequently leads to an erroneous interpretation of the trend of changes in gas concentrations in the composition of mine atmosphere [4]. Coal is a porous medium with diverse character of the pore structure. The occurrence of micropores, mesopores and macropores in coal depends mainly on coal rank and maceral composition [5]. The increase in the total number of micropores corresponds with the increase of coal rank [6]. Micropores dominate in high rank coals whereas in the low rank coals macropores predominate. Macerals are microscopically organic constituents of coal and they are classified as vitrinite, liptinite, and inertinite [7]. It was found that vitrinite characterizes of greater micrporosity than inertinite which is mostly mesoporous [8,9]. Liptinite is the least porous. Thus, the high rank coals, which are rich in vitrinite, have high gas storage capacity. Pores of coal matrix surrounded by a network of natural fractures enhance the flow of gases into the internal surface of coal. The transport of sorbed gases in coal is described by both filtration processes according to Dracy's law and the diffusion processes taking place in the

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macropores and micropores [10,11]. The flow through the networks of fractures is related to the pressure gradient and the swelling in the coal matrix, whereas the flow into the macropores and micropores is driven by the concentration gradient [12]. Under mining conditions, in the dynamic gases flow system, the forces acting on the rock are supported by the grain to grain contact and gas pore stress thus the effective stress is low. With the increase of overburden load, e.g. with increased depth and out flow of the gases from pore spaces, the stress starts to be taken only by grain to grain contact. This phenomenon makes the increase of effective stress and initiates the compaction process leading to a decline in fracture porosity and matrix porosity as well as the permeability [35,36]. Also, a heterogeneous structure of the coal caused by various pore size distribution makes that gases begins to diffuse to the matrix and causes the swelling of the matrix, leading to decrease of permeability [37,38]. Gases flowing through coal may be trapped as an adsorbed layer on the internal surface of coal matrix or as a free gas under pressure resulting from the thermodynamic equilibrium of the system in the fracture structure. The adsorption process in is distinguished as physical adsorption or chemisorption depending on the type of forces between the adsorbate and the adsorbent. The physical sorption occurs quickly and is reversible. It forms a multi-molecular layer and is dominated by a weak van der Waals force. In contrast, chemisorption involves the formation of chemical bonds between the adsorbate and the surface of solid adsorbent and it forms a monolayer. The amount of gas sorbed depends on a number of factors such as temperature, pressure, the nature and the surface area of the adsorbent, as well as the properties of the adsorbant. In general, the amount of gas adsorbed on a given solid surface increases with increasing pressure and with an increase in the surface area of adsorbent. The volume of gas adsorbed for physical sorption decreases with the increase in temperature, while for chemisorptions it increases with the rise in temperature. Numerous studies on the sorption process demonstrated that the amount of sorbed gas depends on the physical–chemical properties of a gas molecule [13,14].

A porous adsorbent behaves like a molecular sieve, so small size molecules are easily enabled to permeate into the micropores which are inaccessible for gases characterizing of larger size. The penetration of larger molecules deep into the microporous structure of coal becomes difficult, and, consequently, the adsorption process cannot occur. Besides, the extent of physical sorption is higher when the gas has a temperature below critical temperature, i.e. the temperature above which the gas cannot liquefy even if the pressure will be increasing. Thus, the gas with higher critical temperature will be more readily sorbed. The amount of chemical sorption is governed by the chemical properties of molecules, in other words, their possibility to form a chemical bond with the solid. For example, alkanes are characterized by lower reactivity than alkenes because of their stable structure, a single covalent and strong sigma (δ) bonds between carbon atoms [15]. Multiple bonds between the two atoms of carbon make unsaturated hydrocarbons more chemically active. The reactivity of hydrocarbons can be related to the energy of the weakest C−H bond. For example, an ethylene molecule has only primary carbon atom yield and gives a vinylic group, meanwhile propylene has both primary and secondary carbon atoms, thus two alkyl groups: vinylic and allylic. The bond energies of allylic and vinylic groups are 361 kJ/mol and 445 kJ/mol, respectively [16]. This is why the energy required to break the bonds in propylene is lower than in the case of ethylene. The selected properties of the tested gases are given in Table 1.

Numerous works examined the adsorption of gases present in the mine during endogenous fire; however, most of them have measured adsorption of single gas in coal [17]. These studies showed that carbon dioxide and acetylene are gases sorbed in the largest amount while the adsorption of carbon monoxide and hydrogen is very small. The extent of the adsorption of ethylene and propylene is slightly smaller. There are many publications about the adsorption of gas mixture on coal [18–22]. Most of them used the mixture of carbon dioxide and methane

Table 1
Properties of the gas used in the experiment.

Gas	Unit	Molecular weight M (g/mol)	Critical temperature T_c (K)	Kinetic diameter d (nm)
Ethane	% w/w	30.07	305.80	0.44
Ethylene	% w/w	28.05	282.30	0.39
Propane	% w/w	44.10	369.80	0.43
Propylene	% w/w	42.08	364.80	0.45
Acetylene	% w/w	26.04	308.30	0.33
Carbon monoxide	% w/w	28.01	134.45	0.38
Carbon dioxide	% w/w	44.01	304.10	0.33
Hydrogen	% w/w	2.02	33.18	0.45

as an adsorbant but only in the context of enhanced coalbed methane recovery. The existing literature provides little information on the sorption of multi-component gas mixture which contains: carbon dioxide, carbon monoxide, ethane, ethylene, propane, propylene, acetylene and hydrogen; particularly if we would like to know more about their transport mechanisms. More researches have measured the adsorption of a hydrocarbon mixture on other materials, for example on zeolite, in the context of the separation of hydrocarbons [23–25].

Under real conditions, the gases released from the source of self-heating of coal constitute a multi-component mixture of oxidation products such as carbon monoxide, carbon dioxide as well as hydrogen, methane and other hydrocarbons e.g. ethane, ethylene, propane and propylene. Therefore, in the sorption measurements the adsorbant should include as large a number the above-mentioned gases as possible in order to better reproduce the mining environment under laboratory conditions. On account of this, the study into the flow of mixture through coal with relation to mixture of fire gases was conducted, particularly since these gases may be selectively sorbed on coal due to their properties. At the same time, the experiment aimed at reflecting in the measurements the real conditions underground where the natural phenomenon such as the flow of gas mixture through porous coal, parallel with the sorption process, may occur during the spontaneous combustion of coal. The idea of simulated self-heating of coal with the application of reactor and the analysis of the mixture composition produced in the reactor by gas chromatograph is not new. In this paper, the idea of combining the process of simulating the coal oxidation under various temperature conditions with the sorption process of these oxidation products on coal is examined, which constituted the fundamental novelty of this experiment.

2. Materials and methods

2.1. Materials

Two coal samples from different coal mines located in the Upper Silesia Coal Basin were used as an adsorbent. The samples were crushed to a grain size ranging from 0.5 to 0.7 mm and from 1.0 to 2.0 mm. A finer coal fraction was packed in the column whereas a larger was used for the oxidation process in the reactor. The results of proximate and ultimate analyses of the examined samples are given in Tables 2 and 3, respectively. The analyses of the samples were carried out in the accredited laboratory of the Department of Solid Fuel Quality Assessment at the Central Mining Institute with the application of the following apparatuses: a) automatic thermogravimetric analyzers LECO: TGA 701 or MAC 500 (moisture, ash and volatiles content), b) TruSpecCHN analyzer LECO (carbon, hydrogen and nitrogen content) and TruSpecS analyzer LECO (sulfur content). The experiments were carried out according to the following Polish standards: PN-ISO 1171:2002 and PN-G-04560:1998 (ash content); PN-G-04516:1998, PN-G-04560:1998 and PN ISO-562:2000 (volatile matter content); PN-G-04511:1980 (total moisture content); PN-G-04571:1998 (carbon, hydrogen and nitrogen