Sorption characteristic of coal as regards of gas mixtures emitted in the process of the self-heating of coal

Karolina Wojtacha-Rychter¹*, and Adam Smoliński²

¹Central Mining Institute, Department of Mining Aerology, Pl. Gwarków 1, 40-166 Katowice, Poland
²Central Mining Institute, Department of Energy Saving and Air Protection, Pl. Gwarków 1, 40-166 Katowice, Poland

Abstract. One of the most challenging tasks in the coal mining sector is the detection of endogenous fire risks. Under field conditions, the distance between the points where samples for the analyses are collected and the actual place where coal self-heating takes place may be quite remote. Coal is a natural sorbent with a diverse character of pore structures which are surrounded by fractures and cleavage planes constituting ideal spaces for the flow and adsorption of gases. The gases (methane, ethane, ethylene, propane, propylene, acetylene, carbon dioxide, carbon monoxide, hydrogen) released from the source of fire migrate through the seam and may be subject to adsorption, or they may cause the desorption of gases accumulated in coal. Therefore, the values of reference sample concentrations may be overstated or understated, respectively. The objective of this experimental study was to investigate the adsorption phenomena accompanying the flow of a multi-component gas mixture through a coal bed which may occur in situ. The research was conducted by means of a method based on a series of calorimetric/chromatographic measurements taken to determine the amount of gases released during coal heating at various temperatures under laboratory conditions. Based on the results obtained in the course of the experiments, it was concluded that the amount of gas adsorbed in the seam depends on the type of coal and the gas. Within the multi-component gas mixture, hydrocarbons demonstrated the largest sorption capacity, especially as concerns propylene.

1 Introduction

Endogenic fire has been one of the most serious types of hazard affecting workers safety, economic loss and environment pollution in coal mining. This phenomenon is a consequence of coal self-heating caused by the accumulation of heat released from the contact of hard coal with oxygen from the surrounding air. A number of techniques based on optical microscopy and thermal studies have been investigated to determine the susceptibility of coal to spontaneous combustion [1-3]; however, in order to evaluate the state of spontaneous combustion, mine operators apply fire indices [4-6]. The concept behind this method is based on the following: 1) the monitoring of mine air composition in selected places underground, 2) the assumption that the profile of the emission of gaseous oxidation products is characteristic of the temperature of the coal, and 3) determining the fire indices as calculated on the basis of the concentrations of gases in mine air. Typical composition of the gas mixture emitted during the coal self-heating process is as follows: carbon monoxide, carbon dioxide, hydrogen, methane, propane and ethane, propylene, ethylene and acetylene. As the temperature of the heating medium increases, the concentration of the above gases in the mine atmosphere increases. The relations between coal temperature, the value of fire indices and gas composition are established during the oxidation of a reference coal sample at different temperature ranges under laboratory conditions. Nevertheless, the results of the test carried out in laboratory condition cannot corresponded with the results obtained under field conditions because gases released from the source of fire migrate through the seam and may be subjected to adsorption or desorption on coal. The distance between the point where samples for the analyses are collected and the actual place where coal self-heating takes place may be quite remote. Since coal represents a fractured porous medium with a diverse character of the pore structure, the pores themselves are surrounded by zones of fractures and cleavage planes which enable gas permeability and adsorption. Gas sorption capacity depends primarily on the presence of micro-pores whereas transport pores i.e. meso-pores and macro-pores, as well as fractures are the decisive factors in gas flow as well as the ability of coal to permeability [7]. The structure of the pores varies with carbon content: the macro-pores dominate in lower rank coals while high rank coals contain mainly micro-pores [8]. Additionally, the geometries of gases molecules strongly affect the selectivity of gas transport in coal. Molecules with the small kinetic diameter can permeate more
successfully [9]. Coal behaves as a binary system due to the presence of hydrophobic and hydrophilic areas on the surface of coal grains. Hydrophobic properties of coal surface are determined by aliphatic/aromatic hydrocarbons fragments of coal structure and fragments containing sulfur atoms (SH groups, thioethers) [10]. Hydrophilic properties of coal surface correlate to the occurrence of numerous active functional groups: methyl, hydroxyl, carboxyl and carbonyl. These groups give the apolar basic mass of hard coal a certain degree of polarity [11]. The ratio of hydrophobic and hydrophilic areas varies depending on the degree of metamorphism. As the carbon content decreases, the oxygen content increases; simultaneously, the number of the hydrophilic areas increases. Consequently, the greatest amount of sorbed gases is observed in the case of coals which are characterized by a low degree of metamorphism. The sorption phenomenon accompanying the flow of gases through a coal bed may affect the values of gases concentrations in coal sample collected under field condition which may be overstated or understated. Research on gas sorption process on coal has been carried out mostly on pure-single gases or gas mixtures within the context of methane recovery. Under real conditions, gases emitted from the source of coal self-heating are a mixture of products characteristic of various temperatures of coal [12]; hence, it is justified to conduct research on the influence of a multi-component gas mixture flow through a coal bed on selected gases concentration in mine air.

2 Materials

For the purpose of the study, three coal samples were collected from the Upper Silesia Coal Basin. The fresh coals used throughout the study were crushed and sieved to grains of size ranging from 0.5 to 0.7 mm and from 1.0 to 2.0 mm. Finer coal fractions were used for the heating of coal in furnace but larger fractions was used as coal bed. Afterwards, the selected fraction of sample was divided to obtain a representative volume by means of the quartering method. Samples were coded with the consecutive numbers: sample 1, sample 2, sample 3. The proximate and ultimate analyses have been carried out on selected samples 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 content), PN-G-04584:2001 as well as PN-ISO 334:1997 (sulfur content), and PN-ISO 7404-3:2001 (maceral groups content and mineral substance content). The results of the analyses of samples in analytical state are presented in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>% w/w</td>
<td>74.66</td>
<td>81.01</td>
<td>64.18</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>% w/w</td>
<td>4.16</td>
<td>4.26</td>
<td>4.13</td>
</tr>
<tr>
<td>Oxygen</td>
<td>% w/w</td>
<td>9.02</td>
<td>6.83</td>
<td>12.78</td>
</tr>
<tr>
<td>Sulfur</td>
<td>% w/w</td>
<td>0.32</td>
<td>0.57</td>
<td>0.85</td>
</tr>
<tr>
<td>Ash</td>
<td>% w/w</td>
<td>7.44</td>
<td>5.06</td>
<td>7.52</td>
</tr>
<tr>
<td>Moisture</td>
<td>% w/w</td>
<td>3.02</td>
<td>1.34</td>
<td>9.69</td>
</tr>
<tr>
<td>Volatiles</td>
<td>% w/w</td>
<td>29.76</td>
<td>28.33</td>
<td>30.55</td>
</tr>
<tr>
<td>Mineral matter</td>
<td>% vol.</td>
<td>1</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Vitrinite</td>
<td>% vol.</td>
<td>45</td>
<td>26</td>
<td>70</td>
</tr>
<tr>
<td>Liptinite</td>
<td>% vol.</td>
<td>11</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Inertinite</td>
<td>% vol.</td>
<td>44</td>
<td>58</td>
<td>22</td>
</tr>
<tr>
<td>Vitrinite reflectance</td>
<td>% vol.</td>
<td>0.76</td>
<td>0.88</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Gas chromatography was used to determine the concentrations of each of the components of the mixture of gases released during the process of coal heating. For the purpose of obtaining optimal detector selectivity and sensitivity, suitable intensities of the carrier gas stream flow along with the temperatures of the detector and column were chosen. High purity argon was used as a carrier gas for hydrogen but in the case of carbon dioxide, carbon monoxide, ethane, ethylene, propane, propylene and acetylene pure helium was applied. The flame ionization detector (FID) was applied to determine ethane, ethylene, propane, propylene and acetylene whereas for determining carbon dioxide, carbon monoxide and hydrogen, the thermal conductivity...
detector (TCD) was used. The compounds were burnt in a hydrogen/synthetic air flame. The application of special concentrator columns enabled to determine trace levels of ethane, ethylene, propane, propylene, acetylene within the scope of low-temperature oxidation.

![Schematic of the set test stand.](image)

### 4 Results and discussion

Experimental data summarized in Figs. 2, 3 and 4 were presented as the percentage of gas sorbed in the coal bed for a given temperature. Based on the results, two characteristic regularities were observed, namely: coal sorption capacity was the highest as regards propylene and acetylene and the lowest in the case of carbon monoxide and hydrogen.

Carbon and oxygen content in coal are the most significant factors determining the behavior of coal with reference to sorbed hydrogen [13]. The percentage of hydrogen molecules in sorbed gas increases along the increase of carbon percentage and the decrease of oxygen amount. It was observed that the highest amount of sorbed hydrogen was gained for coal containing from 70 to 80% of carbon [14]. This behavior reflects the fact that the hydrophobic character of coal surface constitutes a factor which favors the sorption of hydrogen molecules. Furthermore, it has been found that sorption of carbon monoxide is closely related to the number of accessible active sites on coal surface [15]. The number of polar active sites centers in coal is proportional to oxygen content and inversely proportional to its carbon content.

The adsorption of saturated hydrocarbons is lower than the sorption of unsaturated hydrocarbons despite the fact that the concentration of propane and ethane was 2-3 times higher in the inlet gas stream. The sorption mechanism of non-polar molecules of propane and ethane is associated with a dispersion interaction [13, 16, 17]. The varied reactivity of propane and ethane can be related to the energy value of the C-H bond. Table 2 presents the typical bond energies for a C-H bond [18].

<table>
<thead>
<tr>
<th>Energy [kJ/mol]</th>
<th>Primary</th>
<th>Secondary</th>
<th>Tertiary</th>
<th>Allylic</th>
<th>Vinylic</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>.</td>
<td>445</td>
</tr>
</tbody>
</table>

The sorption of unsaturated hydrocarbons: propylene, ethylene and acetylene has been previously discussed in the literature. Multiple bonds between the two atoms of carbon make gaseous substance more chemically active and undergo reactions with polar fragments of the coal structure [19, 20]. A double bond (C=C) in propylene and ethylene has one strong sigma and one weak π bonds; a triple bond (C≡C) in acetylene has one sigma bond with two remaining being π bonds. Additionally, a small size of the kinetic diameter of these molecules enables the gases to permeate to the micro-pores which are inaccessible for gases characterizing of larger kinetic diameters. However, the results of the experiment demonstrate that sorption preference is not always directly correlated with the dimension of the molecule. Acetylene is sorbed in a smaller amount than propylene despite the small kinetic diameter of 0.33 nm (kinetic diameter for propylene is 0.45 nm). Alkenes contain structural fragments characteristic of the alkanes. These groups may react in the same conditions as the alkanes. Hence, the varied reactivity of propylene and ethylene can also be linked to the value of the energy of the C-H bond. Ethylene presents vinylic C-H bond, while propylene has both vinylic and allylic C-H bonds [18]. The energy of allylic bonds is 361 kJ/mol, the energy of vinylic C-H bonds are higher than 400 kJ/mol. It may be therefore assumed that propylene is more reactive with polar fragments of coal than ethylene. To sum up, the difference in the reactivity between the unsaturated hydrocarbons and saturated hydrocarbons could be explained by the reactivity of the carbon-carbon bond and the value of the energy of carbon-hydrogen bond. Alkenes are relatively stable compounds, but are more reactive than alkanes either because of the reactivity of the carbon–carbon π-bond or the presence of allylic C-H bond.

In the literature, the sorption of carbon dioxide was mostly considered in the aspect of enhanced coal bed methane recovery. According to literature [21-23], the CO$_2$ affinity for the coal structure is twice as much as the methane, and methane is readily desorbed from the coal and replaced by carbon dioxide. The phenomenon of preferential carbon dioxide adsorption on natural coals is connected with a linear molecule shape, small size of the kinetic diameter of molecules (0.330 nm), large adsorption affinity (energy), high quadrupole moment and low value of the activation energy [24, 25].
**Fig. 2.** The percentage of gas adsorbed in the coal sample 1.

**Fig. 3.** The percentage of gas adsorbed in the coal sample 2.
Based on the analysis illustrated in Table 1, each sample represented different coal rank group. Sample 3 has the highest carbon content, followed by sample 1 and sample 2. The lowest degree of metamorphism of sample 3 corresponds to the highest oxygen content. It is generally known that coal with low carbon content and high oxygen content has the highest sorption capacity. Sample 3 sorbed acetylene and propylene at all temperatures. Interestingly, despite the high content of mineral matter, low sorption capacity was not observed for sample 3. Most probably, the composition of mineral substance had a positive influence on coal sorption capacity. Similar observations were made by Deng et al. [26] who concluded that mineral composition may influence the volume of pores consequently reducing or enhancing the gas sorption capacity. Additionally, they found that clay, the most commonly occurring inorganic constituent of coals, has strong positive correlation with surface area and pore volumes. The petrographic analysis of coals indicated that sample 3 has the highest content of vitrinite and the lowest content of liptinite and inertinite. Vitrinite group is less porous than inertinite but has high sorption capacity due to its high micropore fraction [27]. This relation may correspond to specific surface area and sorption capacity of sample 3. It was also reported in the literature that vitrinite contains more aromatic components than inertinite and liptinite groups which contain more aliphatic groups [28-30]. The hydrophobic properties differ for each group: aromatic groups are less hydrophobic than aliphatic groups [8]. The sorption capacity of samples 1 and 2 was lower probably as result of the increase in the degree of condensation of aromatic rings in internal vitrinite structure with the increase in coal rank and the decrease in micropores [29].

5 Conclusions

The study on the influence of a multi-component gas mixture flow through a coal bed allowed for the characterization of selective sorption of gases in relation to different coal rank groups. On the basis of the research experiments, it can be concluded that the sorption capacity of coal with respect to multi-component gas mixtures as a sorbate depends on the interaction between gases molecules and coal structure. In the course of the experiment, propylene was sorbed in the largest amount. This could be explained by both the occurrence of the reactivity of the double π-bond (C=C) and the allylic bond (C-H). Carbon monoxide and hydrogen constitute gases which were sorbed in the smallest amounts. The sorption capacity of the three coal samples tested changed depending on the coal rank. Sample 3 with the lowest degree of metamorphism and high content of oxygen as well as vitrinite and mineral matter reveals great sorption capacity. The high content of oxygen indicates that the surface of sample 3 may be strongly hydrophilic due to some oxygen-functional groups present on the coal surface. Test results confirm a positive correlation between mineral matter content and sorption capacity of coal. In conclusion, fire indices calculated on the basis of the concentrations of gases with high sorption ability can be a source of errors due to
the sorption taking place, especially if the coal displays high sorption capacity.

Acknowledgements
This work was supported by the Ministry of Science and Higher education, Poland [grant number 11305117]

References
2. B. Beamish, R. Beamish, Experience with using a moist coal adiabatic oven testing method for spontaneous combustion assessment (Proceeding in 11th Underground Coal Operators Conference, 2011)
12. J. Cygankiewicz, Proceedings of the 4th school of mine ventilation (Section of MineVentilation Committee on Mining Polish Academy of Science, 2006)
18. D. Duprez, F. Cavani, Handbook of Advanced Methods and Processes in Oxidation Catalysis: From Laboratory to Industry (Imperial College Press, 2014)
27. L.A. Harris, Ch.S. Yust, Fuel 55, 3 (1976)
30. A. Ślączka, A. Wasilczyk, Górnic two i Geologia 7, 3 (2012)