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INFLUENCE OF THE METAMORPHISM GRADE AND POROSITY OF HARD COAL ON SORPTION AND DESORPTION OF PROPANE

WPŁYW STOPNIA METAMORFIZMU I POROWATOŚCI WĘGLI KAMIENNYCH NA SORPCJĘ I DESORPCJĘ PROPANU

In this paper results of investigations of sorption of hard coal samples collected from the extracted coal seams of Polish coal mines are presented. As sorbate propane was used. Examinations were carried out in the temperature of 298 K by means of volumetric assessment with the use of apparatus ASAP 2010 of Micromeritics. On the basis of conducted examinations it has been found out that the amount of sorbed propane depend on a type of coal, its metamorphism grade, content of oxygen element, moisture and porosity of these coals. The greatest amounts of propane are sorbed by low carbonized, high-porosity coals of high content of oxygen and moisture. Sorption of relatively high amounts of propane by these coals (ca. 10 cm^3/g) is a result of the influence of polar surface of coals with molecules of propane and good availability of internal microporous structure of these coals for molecules of examined sorbate. Medium and high carbonized coals sorb insignificant amounts of propane. These coals have compact structure and non-polar character of their surface, their internal porous structure is to a minor degree available for propane molecules in conditions of carried out research. Sorption of propane in this case, takes place mainly in surface pores and on the surface of coals. Moreover, measurements of desorption isotherms of propane showing irreversible character of sorption were made. Desorption isotherms do not come together with sorption isotherms forming open hysteresis loop. Amounts of non-desorbing propane remaining in the coal depend on the type of examined coal.

Keywords: hard coal, propane, sorption, desorption

W pracy przedstawiono wyniki badań sorpcji próbek węgli kamiennych pobranych z eksploatowanych pokładów węglowych polskich kopalń. Jako sorbat zastosowano propan. Badania przeprowadzono w temperaturze 298 K metodą objętościową z wykorzystaniem aparatu ASAP 2010 firmy Micromeritics. Na podstawie przeprowadzonych badań stwierdzono, że ilości sorbowanego propanu są zależne od rodzaju węgla, jego stopnia metamorfizmu, zawartości pierwiastka tlenu, wilgoci i porowatości tych węgli. Największe ilości propanu sorbują węgle niskouwęglone, wysokoporowate o dużej zawartości tlenu i wilgoci.

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Sorpcja stosunkowo dużych ilości propanu tych węgli (ok. 10 cm³/g) jest wynikiem oddziaływania polarnej powierzchni węgli z cząsteczkami propanu oraz dobrej dostępności wewnętrznej mikroporowatej struktury tych węgli dla cząsteczek badanego sorbatu. Węgle średnio i wysokouwęglone sorbują niewielkie ilości propanu. Węgle te mają zwartą budowę oraz niepolarny charakter powierzchni, ich wewnętrzna struktura porowata jest w niewielkim stopniu dostępna dla cząsteczek propanu w warunkach przeprowadzanych badań. Sorpcja propanu w tym przypadku zachodzi głównie w powierzchniowych porach i na powierzchni węgli. Przeprowadzono również pomiary izoterm desorpcji propanu wykazując nieodwracalny charakter sorpcji. Izotermy desorpcji nie zbiegają się z izotermami sorpcji tworząc otwartą pętlę histerezy. Pozostające w węglu ilości nie desorbującego się propanu są zależne od rodzaju badanego węgla.

Słowa kluczowe: węgiel kamienny, propan, sorpcja, desorpcja

Introduction

Development of gas chromatography in the recent years and application of modern displacents resulted in that, in the mine air, next to routinely determined oxygen, nitrogen, carbon dioxide, carbon monoxide and methane also contents of hydrocarbons are determined: ethane, ethene, propene and propane. Hard coal beds contain a number of gases, among which methane is dominant, but is it accompanied also by other hydrocarbons, including i.a. ethane and propane. In the paper (Kotarba et al., 1995) it has been found out that contents of lower hydrocarbons originating during the emission of gases from coal beds, reach in some parts of coal seams several dozen percent. Emission of gases from coal seams, mainly methane and accompanying it other hydrocarbons, to mine workings is a frequent phenomenon in coal mines. Sudden, uncontrolled release of gases may pose hazard to mining movement and mining teams working underground.

Emission of hydrocarbons into mining atmosphere is undoubtedly connected with the development of phenomena of self-heating of coal, a consequence of which are dangerous endogenous fires. As a result of these processes increases the temperature of coal seam, causing increase of concentration of emitted hydrocarbons. (Wacławik et al., 2000; Lu et al., 2004). Amounts of released gases depend on the type of coal, its metamorphism grade and the temperature of coal bed and degree of the development of self-heating process. On the basis of content of ethane, ethene, propane and propene in the mine atmosphere also a degree of phenomena development of self-heating of coal is estimated.

The fundamental framework of hard coal is of a character of organic polymer made of aromatic hydrocarbons. The outer shell of these aromas constitutes a system of aliphatic-alicyclic hydrocarbons. In this system there can be distinguished crosslink chains, binding with each other aromatic hydrocarbons domains and non-crosslink chains constituting aliphatic chains, alicyclic compounds not combining aromatic domains (Kreiner & Żyła, 2006). Aromatic hydrocarbons due to the presence of π electrons oscillating in their rings are of polar-hydrophilic character which is expressed by relatively high value of dielectric constant equal 12. Coals with high content of chain hydrocarbons and cyclic non-aromatic systems containing average amounts of carbon element (Jasieńko, 1995) are non-polar – hydrophobic coals, their dielectric constant is almost equal to zero value. Hard coals, next to coal groups, have on their surface oxygen reactive groups of polar nature, including: hydroxyl, carboxyl, carbonyl, methoxyl and etheral groups. The above mentioned groups give the coal structure polar character, and dielectric constant of these coals has value of 3 – 4 (Kreiner & Żyła, 2006).

Attention ought to be also drawn to the presence in coal of well-developed structure of pores, which to a great extent is responsible for sorption properties of this sorbent. In coal, a presence of

all types of pores from the smallest micro and sub-micropores through mesopores to macropores was shown (Czapliński (ed.), 1994). Micro and sub-micropores are located mainly in aromatic polymer and constitute the fundamental sorptive part of hard coal, where the highest amount of gases is collected. Meso- and macropores do not take more significant part in the processes of storage, they are treated as transport artery conveying gas molecules to the system of micro and sub-micropores (Kreiner & Żyła, 2006; Bustin & Clarkson, 1999; Saghafi et al., 2007). Macropores are located at the edges of polymer where they are formed as a result of binding alicyclic and aliphatic hydrocarbons.

Works concerning sorption of lower hydrocarbons on hard coal are rarely conducted. Among the published papers, known are studies referring to ethane sorption (Cygankiewicz etal., 2012), higher hydrocarbons: hexane, heptane, octane (Orzechowska et al., 2008) heptane, heptene (Krzyżanowski & Zarębska, 2007), benzene (Żyła & Krzyżanowski, 2000). The proposed paper addresses the issues of sorption of another hydrocarbon – propane.

1. Experimental part

This paper presents the results of 9 sorption samples of hard coals with varying grades of metamorphism, various oxygen content, humidity and varying porosity while using propane as the sorbate. Coal samples were taken from the currently extracted coal seams. Sorption measurements were performed at temperature of 298 K with the volumetric method using the apparatus of Micromeritics, ASAP 2010. This apparatus is equipped with a pump system that allows to obtain the final vacuum which equals $5.06 \cdot 10^{-7}$ Pa. Samples of hard coal crushed to a grain class 0.5-0.7 mm, before the measurement of sorption isotherms, were degassed at a temperature of 318 K, rinsed several times with helium to facilitate the removal of previously sorbed gases and vapours from the surface of coals.

The chemical and technical analysis of the coal samples is shown in Table 1. Data concerning porosity, the pore volume determined by means of mercury porosimetry and specific surface area calculated from the nitrogen adsorption isotherms at a temperature of 77.5 K and carbon dioxide adsorption at temperature of 298 K were summarized in Table 2.

TABLE 1

Chemical and technical characteristics of coal samples

Constituent content	Symbol	Unit	Samples from the following mines								
			W-1	W-2	W-3	W-4	W-5	W-6	W-7	W-8	W-9
carbon	C_t^a	%	84,24	79,46	89,21	78,62	70,82	57,83	79,02	77,12	66,51
sulphur total	S_t^a	%	0,39	0,32	0,25	0,35	3,50	1,10	0,90	0,54	0,89
sulphur from pyrite	S_p^a	%	0,01	0,07	0,09	0,01	3,20	0,71	0,42	0,22	0,61
hydrogen	H_t^a	%	4,58	4,55	4,61	4,37	3,35	3,37	4,81	4,70	3,93
nitrogen	N^a	%	1,52	1,27	1,66	1,15	1,28	0,87	1,13	0,89	0,91
sulphur from ash	S_A^a	%	0,07	0,22	0,20	0,18	1,27	0,03	0,45	0,25	0,17
sulphur combustible	S_c^a	%	0,32	0,10	0,05	0,17	2,23	1,07	0,45	0,29	0,72
oxygen (calculated)	O_d^a	%	4,58	8,07	1,16	6,17	6,29	11,30	8,29	9,69	11,63
moisture	W^a	%	1,75	3,69	1,32	0,60	1,85	11,11	2,57	3,08	13,95
ash	A^a	%	3,01	2,86	1,99	8,92	14,18	14,45	3,73	4,23	2,35
volatile matter	V^a	%	27,12	30,40	20,88	27,93	29,88	28,39	29,86	31,80	29,73

Total porosity, pore volume determined from mercury porosimetry and values of specific surface area determined from nitrogen sorption (77,5 K) and carbon dioxide sorption (298 K)

Sample	Range (5 – 7500 nm)		S_{BET}, m^2/g	S_{D-R}, m^2/g
	Total porosity, %	Volume pores, mm^3/g		
W-5	2,37	18,18	0,66	103,2
W-4	2,39	18,37	0,36	120,2
W-1	2,81	21,80	0,43	115,8
W-3	3,30	26,10	0,38	135,4
W-2	3,87	28,85	2,34	120,0
W-8	4,05	30,90	1,54	140,4
W-7	5,47	41,60	0,26	97,3
W-9	8,70	68,60	20,66	179,4
W-6	13,55	115,44	189,5	170,1

2. Characteristics of propane

Propane in the elemental state is a colourless and odourless gas. It is heavier than air. In the liquid state the boiling point is –42.20°C and is twice as high as the boiling point of ethane. The increase of this temperature can be explained by the increase of electrostatic interaction forces that occur between molecules of alkanes (the so-called van der Waals forces). These intermolecular forces acting in a system with small distances are the result of polarization-induced of electron clouds present in molecules of saturated hydrocarbons. Temporary imposition of electron clouds can be temporarily inconsistent. One alkane portion of the molecule may have a small excess of electrons in relation to the number of electrons of the other part. Short-term displacements of electrons in the molecule of alkane give it the properties of instantaneous dipole moment. Short-dipole of one molecule can induce temporary dipole moments in neighbouring molecules, which is the reason for the creation of weak forces of electrostatic impact between dipole molecules (Mc Murry, 2000). Electrostatic interaction of polar molecules of propane may also exists on the surface of hard coal, which is characterized by high non-uniformity of the energy resulting from the presence of numerous polar centres on it. The first layer of sorbed molecules is formed on the carbon surface as a result of direct interaction of the polar centres of the coal surface with propane molecules of a temporary dipole character. Another amounts of sorbed propane can form subsequent layers, until the establishment of a multi-layer structure of the sorbed molecules. Between different "layers", there are forces of less impact, as compared to electrostatic interaction of the first layer with surface energy centres of hard coal. This layered system of sorbed molecules can affect the gradual desorption of molecules of propane.

3. Investigations of propane sorption

The drawn isotherm of propane sorption is shown in Figure 1. Taking into consideration the amount of sorbed propane, there can be two sets of isotherms distinguished, mainly those characterized by high and low sorption. The largest amounts of propane are sorbed by coals W-6

and W-9. These coals are characterized by an extremely low content of carbon element (57.83% and 66.51%), a high content of the element of oxygen (11.30% and 11.63%), average hydrogen content (3.37% and 3.93%). At the same time, the structural parameters for these coals are high, the total porosity is (13.55% and 8.70%) respectively, and the specific surface area calculated from sorption isotherms of carbon dioxide determined at temperature of 298 K is (170.1 m^2/g and 179.40 m^2/g) as well as from sorption of nitrogen at a temperature of 77.5 K (189.5 and 20.66 m^2/g). These are coals characterized by the so-called "loose structure" and small clusters of aromatic groups and a large number of surface reactive oxygen groups probably in the form of hydroxyl groups. Sorption of propane in this case occurs both, in surface pore systems as well as in available internal pores of coal.
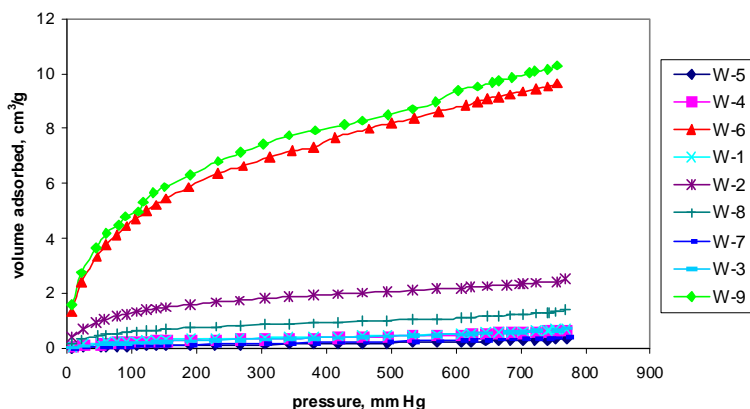
Fig. 1. Isotherms of propane sorption at 298 K on coals samples of different coals of 0,5-0,7 mm particle size

Other coals sorb much smaller amounts of propane. Among these coals the greatest amounts of propane sorb coals W-2 and W-8. These are coals from the borderline of low and medium carbonized coals (79.46% C and 77.12% C) of relatively high oxygen content (8.07% and 9.69%) and a significant amount of hydrogen (4.55% and 4.70%). They are much less porous (3.87% and 4.05%) of average values of surface calculated on the basis of sorption isotherms of carbon dioxide carried out at temperature of 298 K (120.0 m^2/g and 140.4 m^2/g) and sorption isotherms of nitrogen at temp. 77.5 K (2.34 m^2/g and 1.54 m^2/g). These coals have significantly lower amounts of surface oxygen groups and much lower availability of pores for propane molecules compared to coals W-6 and W-9. It is likely that propane sorption in the case of coals W-2 and W-8 takes place on the surface and in the surface pores of coal. Molecules of propane have a relatively large kinetic diameter of 0.43 mm (Xiaochun et al., 2001; Cejka et al., 2005,) and structure, in which the carbon atoms do not form a straight line, but a non-linear one. Movement and then placement of molecules of propane in internal micropores of coal is thereby impeded (Mc Murry, 2000).

Other coals constitute the samples the least sorbing the propane. Propane sorption isotherms of these coals are characterized by a similar course and create a tight band. Sorbed amount of propane are small and do not exceed 0.5 cm^3/g, it is probably the result of surface sorption, the molecules of propane do not penetrate into the micro and sub-micropores of coal. These little

sorbing coals are characterized by medium content of carbon element (78.62 – 89.21% C), small amounts of oxygen (1.16 – 8.29%) and hydrogen and a small percentage of moisture in their natural state, which indicates small numbers of hydroxyl groups on the surface of coal. The structure of these coals is "compact" with a low porosity (2.37 – 5.47%) and a small surface area calculated on the basis of nitrogen sorption isotherms performed at temperature of 77.5 K which, for those coals is included within (0.26 – 0.66 m^2/g). The values of the above mentioned parameters confirm their compact structure, not fully accessible to the molecules of propane in conditions of carried out studies.

In order to illustrate the influence of parameters of coal on the quantity of sorbed propane, the dependencies were shown in the following Figures of the amount of sorbed propane at a pressure about 420 mm Hg on the coal parameters: content of element of carbon, oxygen, moisture, porosity. The influence of the percentage content of the element C on the quantity of sorbed propane was shown in Figure 2. Low carbonized coals sorb much larger quantities of propane, compared to other, higher rank coals. Significant sorption of propane is aided by significant amounts of oxygen polar groups present on the surface of low carbonized coals where polar molecules of propane are bonded by electrostatic interaction forces. Medium and high carbonized coals show a decrease in sorption capacity, which is probably due to "compact structure" and low polar surface of these coals, which is caused by small amount of polar centres on the surface of these coals.
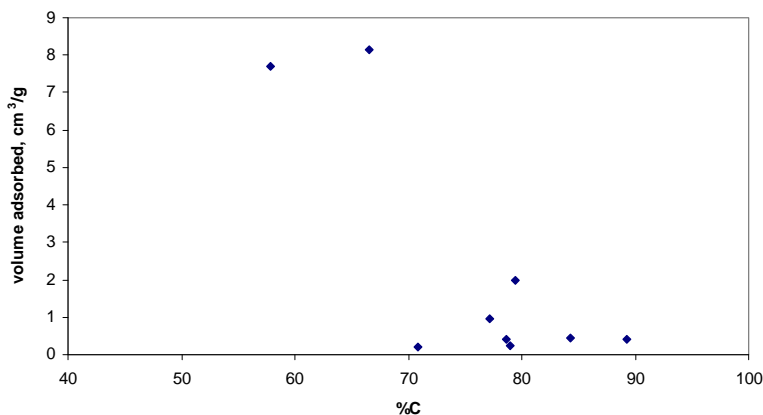

Fig. 2. Changes of volume of propane sorbed at the pressure of 420 mm Hg
as a function of carbon content

The dependence between amount of sorbed propane on oxygen content was shown in Figure 3. Oxygen in coal occurs in the form of reactive oxygen polar groups: hydroxyl, carboxyl, carbonyl and methoxy. The content in coal of oxygen up to 6% does not result in the increase of the amount of sorbed propane; however, coal samples containing more than 6% of oxygen element are characterized by increased propane sorption. This is probably due to the increasing amount of polar oxygen groups, which combine with molecules of propane. Maximum of sorption of propane is attributable to coal samples containing more than 11% of oxygen.
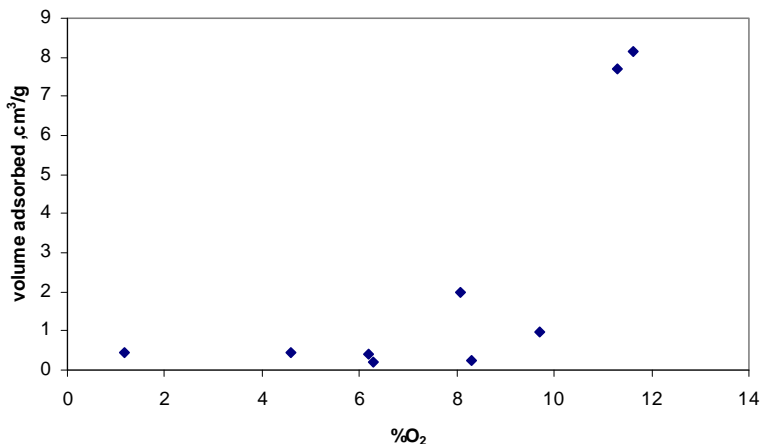
Fig. 3. Changes of volume of propane sorbed at the pressure of 420 mm Hg
as a function of oxygen content

Figure 4 shows the course of the amount of sorbed propane depending on the moisture content in hard coals. Moisture in coal is a consequence of hydrophilicity of coals surface, which is usually due to the presence of polar centres. For coals with a moisture content up to 2%, no increase of sorbed propane amount is observed, only coal samples with a moisture content of more than 2% sorb increased amounts of propane, which is undoubtedly due to the presence of numerous polar centres characterizing these coals. The numbers of these polar centres are present in the structure of very damp coals (moisture content above 11%), which sorb the greatest amount of propane.
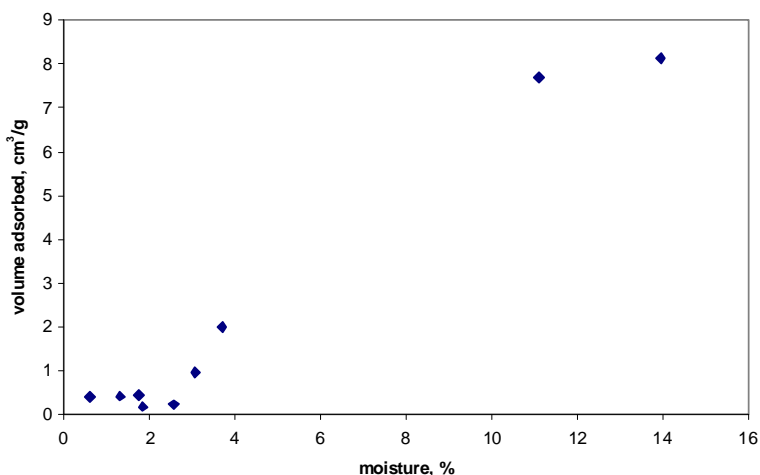
Fig. 4. Changes of volume of propane sorbed at the pressure of 420 mm Hg
as a function of moisture in coal samples

In view of the importance of porosity of coals in the sorption processes, Figure 5 shows the dependency of the amount of sorbed propane on total porosity of coals determined by means of mercury porosimetry. With the increase of coal porosity increases the amount of the sorbed gas. A certain exception is characterized by coal W-7, which, despite increased porosity (5.47%) absorbs small amount of gas. Exceptionally low values of specific surface area of this coal, calculated from the sorption isotherms of nitrogen and carbon dioxide, suggest that the structure of the coal W-7 is poorly accessible to molecules of sorbed propane under the conditions of carried out experiment. Also for coal W-6, a decrease in the amount of sorbed gas, despite its high porosity (13.55%), is observed. Probably, owing to the presence of the large number of inorganic compounds, which form after combustion of coal 14.45% ash.
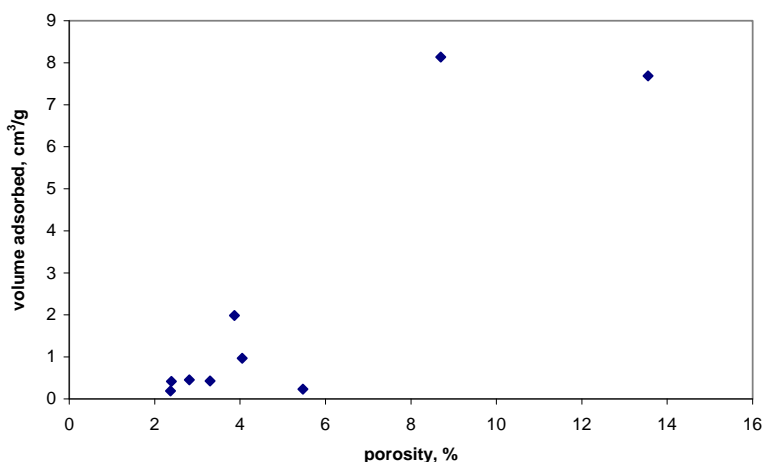
Fig. 5. Changes of volume of propane sorbed at the pressure of 420 mm Hg as a function of total porosity

Summing up the presented dependences it was found that medium and high carbonized coals, little porous, with a moisture content of less than 2%, with insignificant quantity of oxygen element, sorb small quantities of propane. Its compact structure is not available for molecules of sorbed propane. Larger quantities of propane are sorbed by low rank coals with increased porosity, having oxygen content above 6% and above 2% moisture.

4. Investigations of desorption of propane

Phenomenon of desorption is characterized with passage of molecules of desorbed gas from the surface of solid body to gaseous phase situated in the neighbourhood of solid body. The process of desorption of molecules of sorbed substance is endothermic phenomena. Desorption of the sorbed molecules can be carried out by rising the ambient temperature or else, by lowering the concentration of sorbate molecules in sorbent environment.

In the presented investigations desporption was carried out by lowering the concentration of molecules in gaseous phase of the adsorbent – sorbate system. This type of desorption takes

place slowly, since molecules of sorbed sorbate are slowly transformed from the surface of solid body to gaseous phase. Desorption conducted with a method of lowering the concentration of gaseous phase is not only slow but in many cases not completely reversible. In Fig. 6-7, a course of sorption and desorption isotherms was presented, performed for two low carbonized type of coals: W-6, W-9 distinguished by the considerable amount of desorbed propane. Determined desorption isotherms do not converge with sorption isotherms and form open hysteresis loop. Such arrangement of sorption and desorption isotherms is characteristic for the system in which polar centres of coal retain substantial amount of sorbed molecules of propane. Two coals under discussion are distinguished by high surface polarity which contributes to the increased and permanent binding of molecules of propane. Amounts of propane remaining in the structure of coal constitute almost one third of the total amount of sorbed propane.
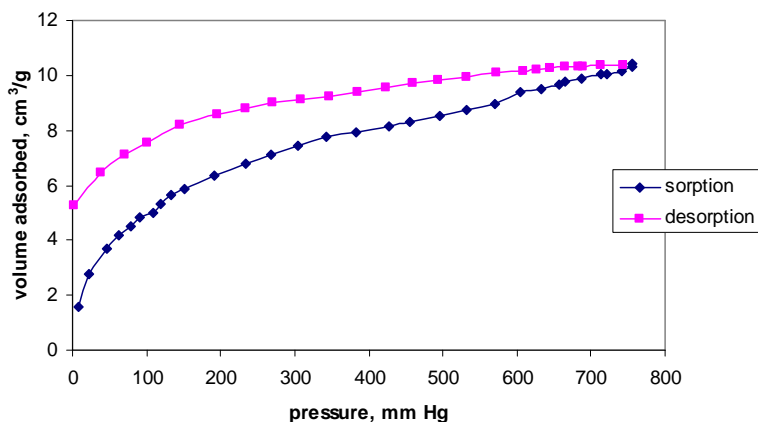
Fig. 6. Isotherms of sorption and desorption of propane in W-9 coal sample of 0,5-0,7 mm particle size determined at 298 K
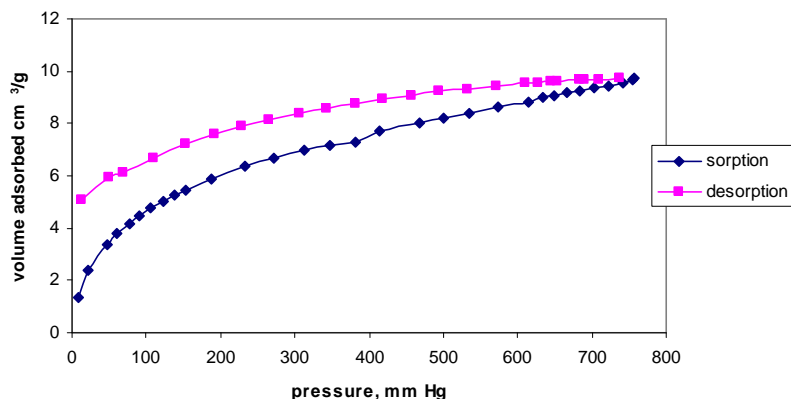
Fig. 7. Isotherms of sorption and desorption of propane in W-6 coal sample of 0,5-0,7 mm particle size determined at 298 K

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In addition, large hysteresis loop is formed by isotherms of sorption and desorption of propane determined on coals W-2 and W-8 (Fig. 8-9). It has been shown that in the case of coal W-2 after conducted desorption about a half of propane remains in the structure of hard coal. Similar amount of propane remains in coal W-8.
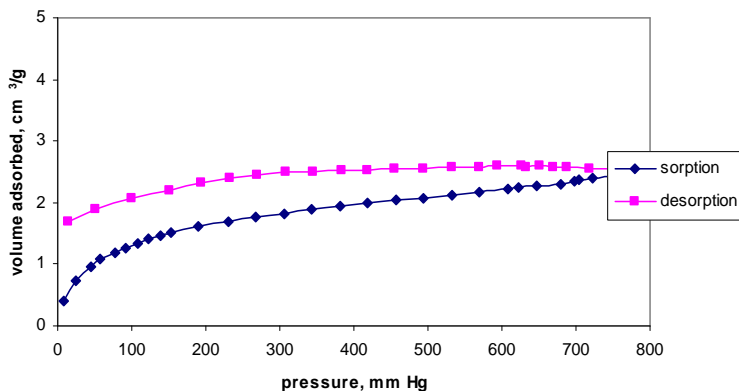

Fig. 8. Isotherms of sorption and desorption of propane in W-2 coal sample of 0,5-0,7 mm particle size determined at 298 K
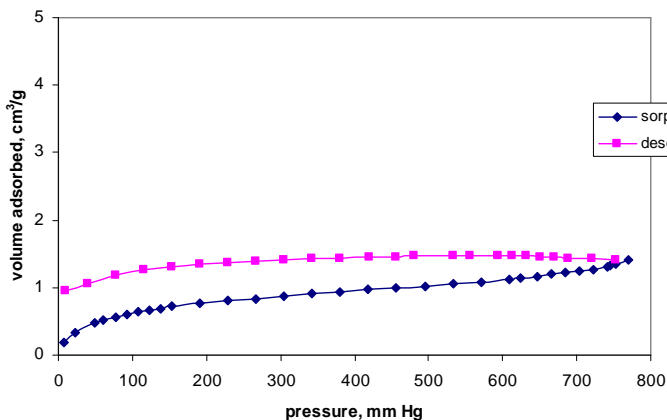

Fig. 9. Isotherms of sorption and desorption of propane in W-8 coal sample of 0,5-0,7 mm particle size determined at 298 K

Another issue that ought to be discussed separately is desorption carried out on five samples of medium-rank coal. The obtained systems of sorption-desorption isotherms are characterized with similar course. Exemplary sorption and desorption isotherms are presented in Fig. 10-12.

In case of these coals, only insignificant amount is sorbed, mainly in the scope of very low pressures. Almost in the whole scope of propane desorption very small amounts of desorbed

propane are observed. It can be assumed that only surface sorbed molecules desorb at gradu-ally decreased pressure. Only at very low pressures of propane, slight approach of desorption isotherms to sorption isotherms is visible. Such course of isotherms indicates the phenomenon of desorption of molecules taking place solely in the external surface of coal. The remaining amounts of sorbed propane present inside the pores of coal have too small kinetic energy to be released from the interior of pores and place itself in gaseous phase surrounding the surface of coal sorbent. In order to provoke the other molecules of propane to desorb it would be advisable to introduce a specific amount of thermal energy to sorbing system. This energy could increase the kinetic energy of molecules, and after overcoming binding forces cause their desorption into gaseous phase.

Conducted research on propane sorption allowed to draw the following conclusions.
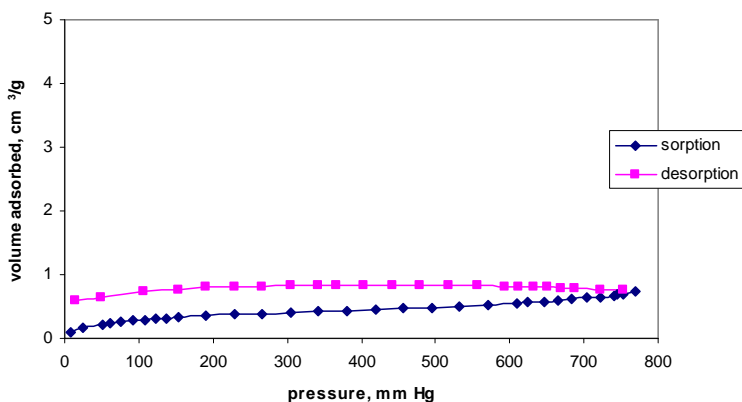
Fig. 10. Isotherms of sorption and desorption of propane in W-1 coal sample of 0,5-0,7 mm particle size determined at 298 K
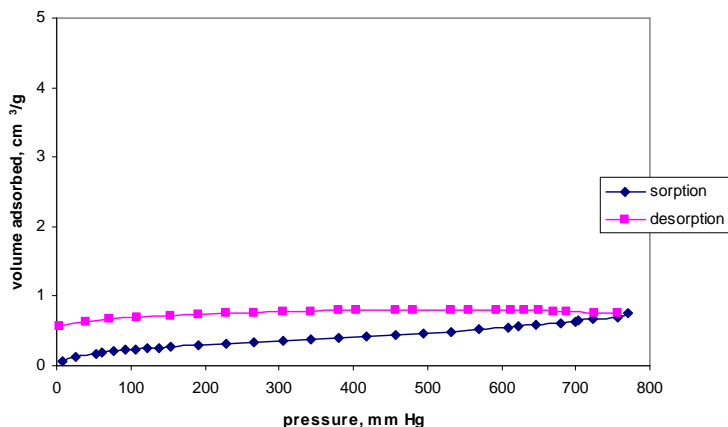
Fig. 11. Isotherms of sorption and desorption of propane in W-3 coal sample of 0,5-0,7 mm particle size determined at 298 K
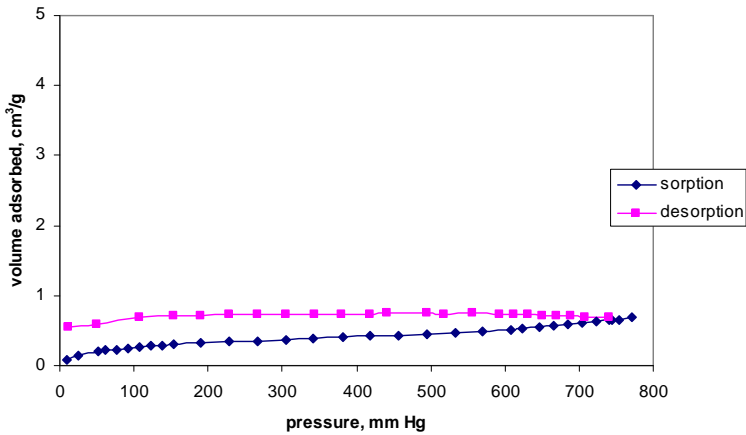
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Fig. 12. Isotherms of sorption and desorption of propane in W-4 coal sample of 0,5-0,7 mm
particle size determined at 298 K

5. Conclusions

1. Low carbonized coal characterized with the so-called „loose structure", presence of polar centres of sorption and good availability of micro and mesopores structure sorb substantial amounts of propane.
2. Medium and high carbonized coals show minor sorption of propane. Internal porous structure of this coal is inaccessible for molecules of sorbed propane.
3. Amounts of sorbed propane depend on metamorphism grade of coal, its porosity and content of oxygen element and moisture. The largest amounts of propane are sorbed by low carbonized, high-porosity coals with high content of oxygen and moisture.
4. The process of sorption of propane is irreversible system. Desorption isotherm does not come together with sorption isotherm forming open hysteresis loop of sorption. In the structure of coal remain various amounts of propane articles, which depends on the type of coal.

References

Bustin R.M., Clarkson C.R.,1998. *Geological controls on coalbed methane reservoir capacity and gas content*. International Journal of Coal Geology 38, 3-26.

Cejka J., Zilkova N., Nachtigall P. (editors), 2005. *Molecular Sieves*. From Basic Research to Industrial Applications, Elsevier.

Cygankiewicz J., Żyła M., Dudzińska A., 2012. *Wpływ stopnia metamorfizmu węgli kamiennych na sorpcję i desorpcję etanu*. Karbo 3/2012

Czapliński A., 1994. *Węgiel kamienny*. Kraków, Wydawnictwa AGH.

Jasieńko S., 1995. *Chemia i fizyka węgla*. Oficyna wydawnicza Politechniki Wrocławskiej, Wrocław.

Kotarba M., Pękała Z., Daniel J., Więcław D., Smolarski L., 1995. *Opracowanie modeli oraz bilansu generowania i akumulacji gazów w serii węglonośnej Górnośląskiego Zagłębia Węglowego*. Red. R. Ney i M. Kotarba. Wyd. Centrum PPGSMiE PAN, Kraków, 61.

Kreiner K., Żyła M., 2006. *Binarny charakter powierzchni węgla kamiennego*. Górnictwo i Geoinżynieria 2, 19-33.

Krzyżanowski A., Zarębska K., 2007. *Sorpcja par cieczy apolarnych na węglu kamiennym o różnym składzie petrograficznym*. Gospodarka Surowcami Mineralnymi, 23, 175-181.

Lu P., Liao G.X., Sun J.H., Li P.D., 2004. *Experimental research on index gas of the coal spontaneous at low-temperature stage*. J. Loss Prevention in the Proc. Industries 17, 243-247.

Saghafi A., Faiz M., Roberts D., 2007. *CO_2 storage and gas diffusivity properties of coals from Sydney Basin, Australia*. International Journal of Coal Geology 70, 240-254.

Mc Murry J., 2000. *Chemia organiczna*. Wydawnictwo Naukowe PWN Warszawa.

Orzechowska-Zięba A., Nodzeński A., 2008. *Chłonność sorpcyjna węgla kamiennego względem węglowodorów $C_6 - C_8$*. Gospodarka Surowcami Mineralnymi, 24, 3, 245-254.

Wacławik J., Cygankiewicz J., Branny M., 2000. *Niektóre zagadnienia pożarów endogenicznych*. Biblioteka Szkoły Eksploatacji Podziemnej, Seria z Perlikiem nr 2, 33-35

Xiaochun X., Weishen Y., Jie L., Liwu L. 2001. *Synthesis of NaA zeolite membranes from clear solution*. Microporous and Mesoporous Materials 43, 299-311.

Żyła M., Krzyżanowski A., 2000. *Wpływ aromatycznej struktury węgli kamiennych na sorpcję par benzenu i jego pochodnych alkilowych*, Karbo, 11, 354-357.