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METHANE RECOVERY FROM GASEOUS MIXTURES USING CARBONACEOUS ADSORBENTS

POZYSKIWANIE METANU Z MIESZANIN GAZOWYCH ZA POMOCĄ ADSORBENTÓW WĘGLOWYCH

Methane recovery from gaseous mixtures has both economical and ecological aspect. Methane from different waste gases like mine gases, nitrogenated natural gases and biogases can be treated as local source for production electric and heat energy. Also occurs the problem of atmosphere pollution with methane that shows over 20 times more harmful environmental effect in comparison to carbon dioxide. One of the ways utilisation such gases is enrichment of methane in the PSA technique, which requires appropriate adsorbents. Active carbons and carbon molecular sieve produced by industry and obtained in laboratory scale were examined as adsorbent for methane recuperation. Porous structure of adsorbents was investigated using densimetry measurements and adsorption of argon at 77.5K. On the basis of adsorption data, the Dubinin-Radushkevich equation parameters, micropore volume (W_o) and characteristics of energy adsorption (E_o) as well as area micropores (S_{mi}) and BET area (S_{BET}) were determined.

The usability of adsorbents in enrichment of the methane was evaluated in the test, which simulate the basic stages of PSA process: a) adsorbent degassing, b) pressure raise in column by feed gas, c) cocurrent desorption with analysis of out flowing gas. The composition of gas phase was accepted as the criterion of the suitability of adsorbent for methane separation from gaseous mixtures. The relationship between methane recovery from gas mixture and texture parameters of adsorbents was found.

Keywords: carbonaceous adsorbents, densities and structural properties, PSA

Odzyskiwanie metanu z mieszanin gazowych posiada zarówno aspect ekonomiczny jak i ekologiczny. Metan pochodzący z gazów kopalnianych, gazów zaazotowanych oraz biogazów może być traktowany jako lokalne źródło do wytwarzania energii elektrycznej i cieplnej. Jest także problemem zanieczyszczenie atmosfery metanem, który ma ponad dwudziestokrotnie większy wpływ na środowisko w porównaniu z ditlenkiem węgla. Jednym ze sposobów wykorzystania tego typu gazów jest wzbogacanie metanu techniką PSA, która wymaga odpowiednich adsorbentów. Węgle aktywne oraz węglowe sito molekularne wytwarzane przemysłowo i te otrzymane w laboratorium były oceniane jako adsorbenty do wzbogacania metanu. Porowata struktura adsorbentów była analizowana za pomocą pomiarów gęstości i adsorpcji

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argonu w temperaturze 77.5K. Z danych adsorpcyjnych wyznaczono, posługując się równaniem Dubinina i Raduszkiewicza parametry: W_o, E_o, S_{mi}, a powierzchnię S_{BET} z równania adsorpcji wielowarstwowej Brunauera, Emmetta i Tellera. Przydatność adsorbentów do wzbogacania metanu była oceniana w teście, który symulował podstawowe etapy procesu PSA; a) odgazowanie adsorbentu, b) podnoszenie ciśnienia w kolumnie gazem zasilającym, c) desorpcja współprądowa połączona z analizą gazu. Skład fazy gazowej przyjęto jako kryterium przydatności adsorbentów do wydzielania metanu z mieszanin gazowych. Stwierdzono zależność pomiędzy stężeniem metanu a porowatą strukturą przebadanych adsorbentów.

Słowa kluczowe: adsorbenty węglowe, właściwości densymetryczne i strukturalne, PSA

1. Introduction

Environmental pollution and implementation of new highly effective technologies raise the interest in potential application of porous carbonaceous materials in enrichment, separation and purification of gaseous mixtures.

Active carbons, of more than one century long history of production and application on the industrial scale as well as the relatively new adsorbents, like carbon molecular sieves and active carbon fibres, may be accounted into this category. There characteristic features a high content of elemental carbon, a developed internal porosity and a high specific surface area make them good adsorbents of molecular components of gaseous or liquid mixtures.

One of the important technological problems addressed last decades is methane extraction in the pure or enriched form (the substitutes of natural gas) from the gases of low methane content. Such potential methane sources are: mine gases, accompanying coal beds, containing 30 to 50% methane, biogases from the anaerobic decomposition of organic materials or landfill gases, as well as a nitrogenated natural gas. The above-mentioned gaseous mixtures may be separated using adsorptive techniques, first of all the pressure swing adsorption (PSA) (Baron, 1994; Olajossy, 2007).

The basic condition, enabling enrichment of the gaseous mixtures in a desired component is the choice of a suitable adsorbent, capable of preferential adsorption of the component on a kinetic or equilibrium basis (Sheikh et al., 1996; Bałys et al., 2002; Olajossy, 2012).

The present studies concern, as example: i. The separation of methane and nitrogen from binary mixtures using a commercial activated carbon was investigated. Activated carbon Norit RB3 exhibited equilibrium selectivity for CH_4 over N_2 in the range 3 to 7, while the mass transfer coefficients of CH_4 and N_2 were similar for this carbon, ranging from 0.004 to 0.052 s^{-1}. The results presented can serve as a reference data set upon which industrial PSA processes for separating $CH_4 + N_2$ mixtures using commercial activated carbon can be developed and optimized. [Rufford at al. 2013], ii. Adsorption and separation of CO_2/CH_4 were examined on to kind of amorphous silica molecular sieve, ASMS-3A and ASMS-SA. For ASMS-3A, the exclusions of CH_4 molecules due to their dimensions into the narrow necks and preferential adsorption of CO_2 with the smaller kinetics diameter is observed at 283K Then ASMS-3A is a promising adsorbent for the separation and purification of CO_2 from various mixtures such a natural gas and landfill gas by PSA process (Morishige, 2011), iii. Vacuum pressure swing adsorption (VPSA) process that uses activated carbon as an adsorbent to recover CH_4 from mixture (70% N_2 and 30% CH_4) was investigated through dynamic optimalization and sensitivity analysis. Under optimal conditions, the purity of CH_4 reaches 80% in the product gas, the recovery of CH_4 is 97%, and power

consumption is 0.186 KWh/Nm^3. Analysis of the sensitivity data provides significant influence into the effects of the operating parameters for the process (Yang at al., 2014).

The aim of this work was to study the attempt to describe carbonaceous adsorbents, enabling methane enrichment in the equilibrium PSA process, from low concentrated mixtures e.g. mine gases, nitrogenated gas and biogas.

2. Materials

Investigations were carried out on commercial active carbons: AG produced by HPSDD Hajnówka in Poland and RN (2RLextra) manufactured by Norit in Holland. Above active carbons were subjected separately to abrasion for a chosen length of time (Buczek, 1993). As result of attrition in spouted bed following products were obtained AG80 and RN80. Carbon molecular sieve CMS (Carbotech BF-H2), originally used for hydrogen purification and enrichment of mine gases, was also under investigation (see Figure 1a-e).
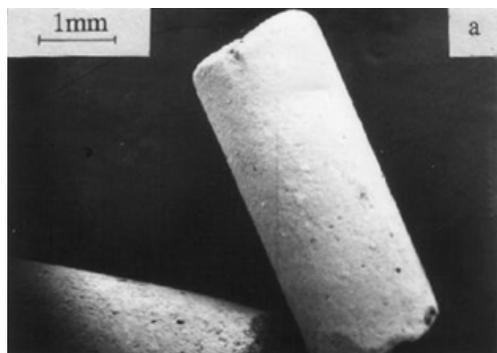

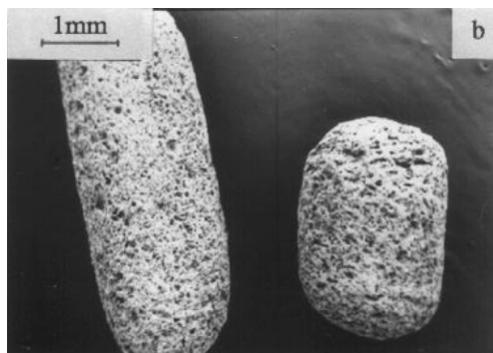Fig. 1a. Scanning microscope picture of AG active carbon

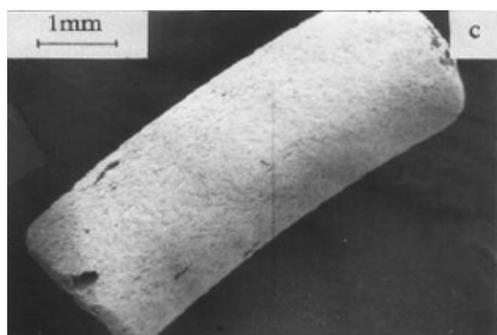Fig. 1b. Scanning microscope picture of AG80 active carbon

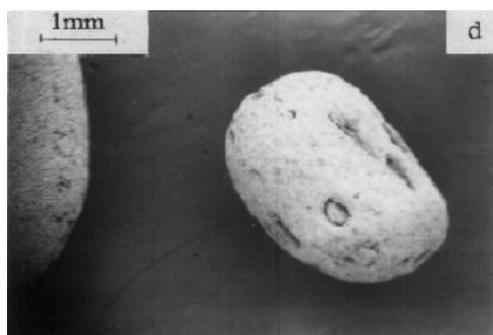Fig. 1c. Scanning microscope picture of RN active carbon

Fig. 1d. Scanning microscope picture of RN active carbon

Fig. 1e. Photograph of CMS carbon molecular sieve

3. Experimental and discussion

Densities and porosity

The development of the porous structure was evaluated basing on density measurements. Apparent (ρ_a) and real (ρ_r) densities were determined for active carbons AG, RN, AG80, RN80 and CMS. The apparent density was measured with mercury and the real one with helium displacement at 293K using equipment described by (Czapliński & Lasoń, 1965). The particle porosity ρ_p and pore volume, accessible to helium (V_o) were calculated from the measurements of true and real densities. The relevant results are presented in Table 1.

TABLE 1

Properties of active carbons and carbon molecular sieve

Adsorbent	ρ_a [g/cm³]	ρ_r [g/cm³]	V_o [cm³/g]	ε_p [cm³/cm³]
AG	1.356	1.955	0.226	0.306
AG80	1.214	1.996	0.322	0.392
RN	1.159	2.033	0.370	0.430
RN80	1.154	2.040	0.376	0.434
CMS	1.024	1.965	0.467	0.479

From the comparison of the pore volume (0.467 cm³/g) and porosity (0.479 cm³/cm³) of the carbon molecular sieve with active carbons it results that above properties are developed to a variable degrees. Porosity and pore volume of RN80 active carbon is comparable with that of the CMS adsorbent. The usability of carbonaceous material in enrichment of methane containing gases is however determined not by total volume of all kinds of pores but by the presence of the definite texture, mainly the microporous one.

Argon adsorption

For characterization of porous structure the adsorbents, isotherms of argon at 77.5K were determined. On the basis of argon adsorption data, the values of Dubinin-Radushkevich equation parameters (Dubinin, 1987), micropore volume (W_o) and characteristics of energy adsorption (E_o, B) as well as area micropores (S_{mi}) and BET area [S_{BET}] were determined (Jankowska et al., 1991). The results of calculations are presented in Table 2.

TABLE 2

Parameters of porous structure of active carbons and carbon molecular sieve

Adsorbent	W_o [cm³/g]	E_o [kJ/mol]	$B*10^6$ [K⁻²]	x [nm]	S_{mi} [m²/g]	S_{BET} [m²/g]
AG	0.30	21.0	0.83	0.58	525	886
AG80	0.28	21.7	0.78	0.55	517	769
RN	0.45	21.4	0.80	0.56	792	1281
RN80	0.41	20.9	0.84	0.58	695	1133
CMS	0.27	23.2	0.68	0.50	540	608

Where x was calculated from equation: $2x = 4.691 \exp(-0.0666 E_o)$ (Mc Enaney, 1987) then $S_{mi} = W_o/x$.

Real applicability of adsorbents for enrichment of methane containing gases may be evaluated in the test simulating the equilibrium PSA process.

4. Testing of adsorbents in the PSA process conditions and discussion

One of the methods widely applied for separation of mixtures of poorly condensing gases is pressure swing adsorption (PSA) (Suzuki, 1990). It is applied in industry for the production of: oxygen and nitrogen from air, hydrogen from gases after reforming process, as well as for separation of various hydrocarbons.

In the case of mixtures such as nitrogen containing natural gas or mine gases, the enrichment consists practically of methane separation from nitrogen and oxygen. Previous investigations showed that the best separation of these gases might be obtained on carbonaceous adsorbents with an appropriate porous structure, making use of differences in adsorption isotherms of individual components of the mixtures (Baron, 1994).

Methane is much better adsorbed on carbonaceous adsorbents than nitrogen. This difference in adsorption capacity determines the course of pressure swing adsorption. Thus, methane recovery proceeds in the stage of counter current desorption, while its enrichment is caused by nitrogen removal during co current desorption. The amount of removed nitrogen, and thus gas phase enrichment in methane depends on adsorptive and separative properties of the adsorbent.

In order to evaluate the suitability of adsorbents for enrichment of methane-containing gases the estimation method based on measurements under conditions simulating the basic stages of PSA process was developed (Buczek, 1996).

The fact that the microporous structure of both investigated active carbons changes radially led to the studies of their separation properties towards the nitrogen-methane mixture. Active

carbons (AG, RN) and their samples in the form of internal cores devoid of 80 wt.% of the surface layers (AG80, RN80) were investigated under increasing pressure and during desorption. For comparison, commercial carbon molecular sieve (CMS), used in pilot plant for enrichment of mine gases (Bałys et al., 2000) was also estimated.

The standard experiment consisted of the following operations: i) adsorbent degassing in a test column down to several mbar; ii) the increase of pressure of the column up to 0.3 MPa, with the supplying gas containing 50% methane and 50% nitrogen; iii) desorption of gas from the column up to 0.1 MPa with the simultaneous analysis of the composition of the out flowing gas. The diagram of the experimental equipment is presented in Figure 2.
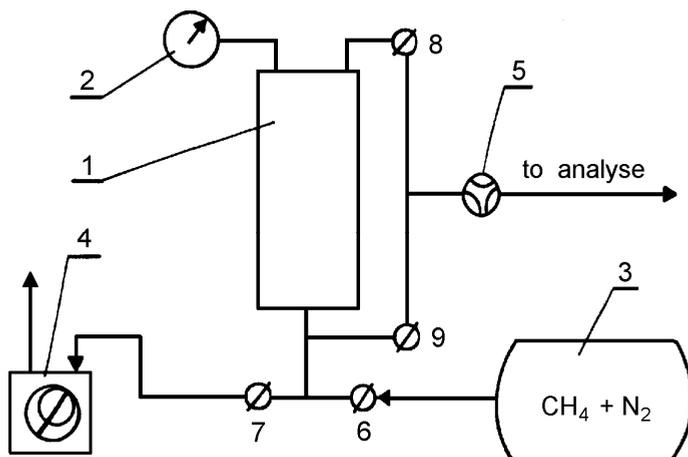

Fig. 2. The experimental equipment for the estimation of the separation properties of the adsorbents under study: 1-adsorbent containing column; 2-manometer; 3-gas container; 4- vacuum pump; 5 six-way valve; 6-9 valves

The equipment enables one to determine gas phase content in the outlet part of the column as a function of pressure during either the co current (through valve 9) or counter current (valve 9) gas desorption.

The column filled with an adsorbent was degassed, supplied with the mixture to be separated and desorption was started. The samples of desorbed gas were analysed, with simultaneous recording of the pressure in the column. The obtained results in the form of methane concentration in the outlet part of the column versus pressure during desorption are shown in the Figure 3.

The experimental curves show a considerable differentiation in separation abilities of the studied adsorbents which forms a sequence: CMS > RN > AG. RN80 and AG80 samples have better separation properties than the initial active carbons. It indicates that the interior of active carbon particles has a porous structure similar to that of carbon molecular sieve.

Basing on both experimental and curve theoretically calculated from the equilibrium model of PSA process (Valenzuela & Myers, 1989), the separation coefficient k, was evaluated for the studied adsorbents to be: 2.9; 3.5, for AG and AG80, 3.2; 3.7, for RN and RN80 and 5.1 for CMS, respectively.

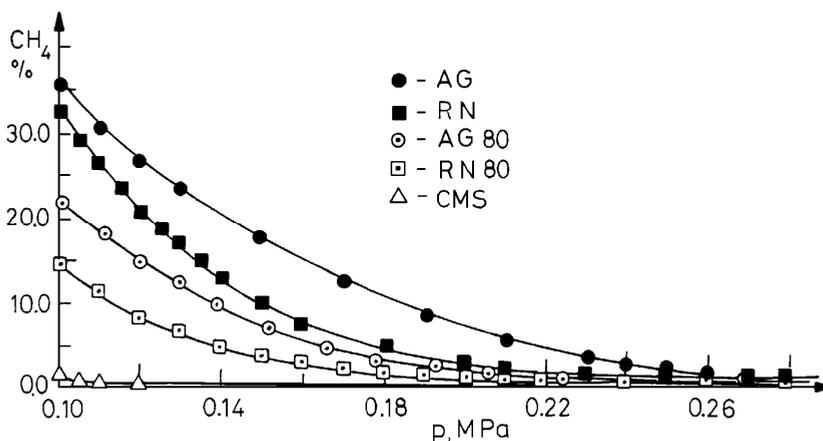Fig. 3. Composition of desorbed gas depending of the outlet pressure for AG, AG80, RN, RN80
and CMS adsorbents

5. Conclusions

The quantitative estimation of separation ability, based on the determination of the coefficients k, enables one to estimate of suitability of a particular adsorbent for methane enrichment in the swing pressure process. It may be seen from calculations it results that the adsorbents with k equal to about 5.0 it make possible obtain practically pure nitrogen during desorption stage. The investigated active carbons, despite of their well developed porous structure, show the inappropriate separation properties and practically are not suitable for the enrichment in methane, which concentration during adsorption reaches 30 and more percent. One may, however, obtain adsorbents of middle separation coefficients (3.5 and 3.7) from the same active carbons, which may be used for methane enrichment up to about 70-80%, if CH_4 concentration in the desorbed gas does not exceed 20%.

Acknowledgements

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