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VEHICULAR APPLICATIONS OF SOLID SORBENTS FOR NATURAL GAS STORAGE

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The state of the art of vehicular applications of solid sorbents for storage of natural gas is analyzed. Experimental data on methane sorption by activated carbon fiber at temperatures from -40 to $+40^oC$ and pressures up to 4 MPa are reported. Owing to the sorbent application the gas cylinder used provides a decrease in the working pressure and an increase in the volume density of storage as compared to systems based on compressed natural gas.

1. Solid Sorbents for Storage of Natural Gas. The increasing consumption of petroleum accompanied by reduction of its stock and ecological problems have commanded the wide use of natural gas as motor fuel, especially in the last twenty years.

The high metal content of vessels for storage of compressed natural gas and the growth of energy consumption for liquation or compression call for other means of natural-gas storage for vehicles.

At present extensive investigations of solid sorbents for natural gas storage are being carried out. One of the reasons for the interest in these materials is the fact that when they are used as fillers of gas cylinders, the natural gas is stored in adsorbed form at reduced pressures without decreasing the volume for the gas. The application of sorbents can allow reduction of the metal consumption for manufacture of gas cylinders and of the energy consumption for gas compression, saving the cost of compression equipment, which is the main expenditure in the production of compressed natural gas.

Pioneering works devoted to methane sorption at elevated pressures were carried out more than 70 years ago in connection with the use of adsorption as a general-purpose method for separation of vapor-gas mixtures and for cleaning and drying of natural gas. In the 1940s at the Mining Institute of the USSR Academy of Sciences V. T. Pavel'ev [1, 2], guided by Academician Dubinin, conducted an experimental study of methane sorption at pressures of from 0.1 to 100 MPa and at a temperature of 25°C for two samples of activated carbon of different structures, i.e., of grades AG2 and F-23. The data obtained revealed that the methane adsorption capacity of the carbon abruptly increases with pressure up to 5–6 MPa and attains its maximum at 0.182 m^3/kg.

Information is available about sorbents which provide a 5–10-fold increase in methane capacity. For example, the firm "Union Carbide" recommends a carbonaceous powder as a filler [3], owing to which the gas is kept at a pressure of 3.5 MPa without decreasing the volume as compared to that of the gas compressed at a pressure of 20 MPa. The patent [4] describes the method of increasing the storage density (gas mass per unit volume of storage) of methane in an automobile by a factor of 10 at room temperature and at a pressure of 1 MPa owing to a solid sorbent placed in the fuel tank. The "Ford" company [5, 6] has developed pilot adsorbents and cylinders which at a pressure of 2 MPa contain a gas stock equivalent of 15 MPa gas cylinders.

In the USA [7-9] a flat automobile tank filled with a pressed carbon sorbent has been developed and manufactured. At a pressure of 3.5 MPa, such a container can provide a volume storage density (the ratio of the gas volume contained in the vessel under normal conditions to the vessel volume) of natural gas of up to 150 nm^3/m^3.

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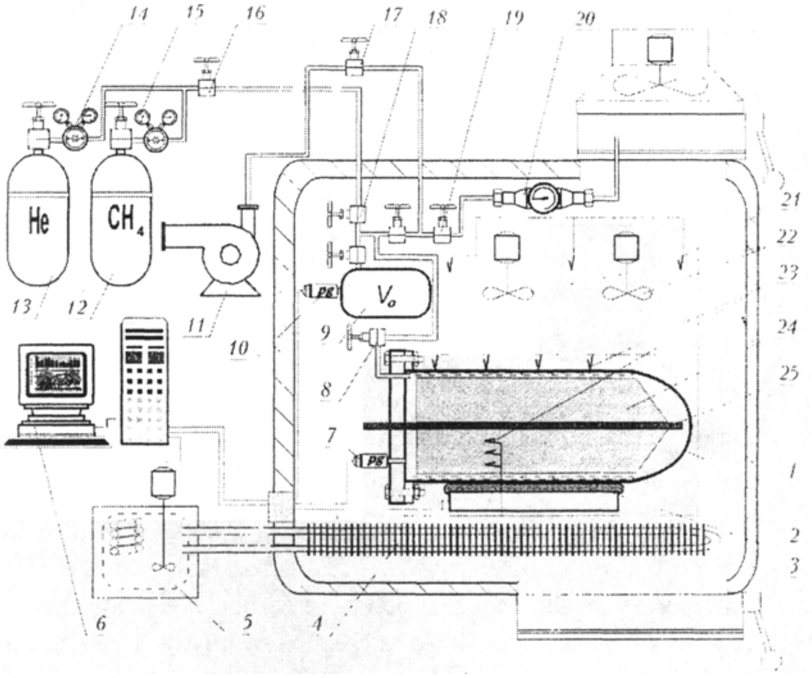


Fig. 1. Diagram of experimental setup: 1) experimental vessel; 2) electronic balance; 3) safety chamber; 4) liquid heat exchanger; 5) thermostat; 6) measurement unit and computer; 7, 10) pressure transducers; 8, 16, 17, 18, 19) valves; 9) calibration space; 11) vacuum pump; 12) methane cylinder; 13) helium cylinder; 14, 15) pressure regulators; 20) flow rate meter; 21) thermocouples inside the chamber; 22) fans inside the chamber; 23) thermocouples; 24) sorbent layer; 25) heating element.

Great efforts of investigators have gone into determination of the methane sorption capacity of different solid sorbents suitable for filling of vehicule gas cylinders [10-16]. In [17] a comprehensive study of the physicochemical and sorption characteristics of activated carbon of seven grades was performed in a pressure range of 1–6 MPa at a temperature of 298 K. The measurement results for the methane adsorption capacity of activated carbon with particles sized from 0.385 to 1.5 mm and a layer porosity of 0.265–0.454 have demonstrated the possibility of increasing the density of methane storage in adsorbed form (48–62 kg/m^3) by a factor of two against that of the compressed gas at the same pressure.

The patents [18-21] point to the positive influence of increasing the carbon bulk density and, consequently, of the presence of particles of different sizes on the amount of adsorbed methane. In the patent [15] it is recommended that a cylinder be filled with carbon particles of at least two sizes with a diameter ratio of 7:1. A high-density adsorbent obtained by compaction of carbon particles with a highly developed surface [20] provides an increase in the density of gas storage by 20–100% as compared to loose filling. The compaction pressure must be sufficient to provide a 1.5–2-fold decrease in the volume of loose material and a corresponding increase in density by 50–100%.

In [22-25] an attempt is undertaken to obtain special-purpose activated carbon for storage of natural gas in adsorbed form. A high microporosity and density and low cost are the most important characteristics of sorbent-fillers of vehicule cylinders. Patent [26] describes a technique for increasing the surface alkalinity of activated carbon, which favors the adsorption of methane. The "Gas Light Company" [27] provides a technology of microporous activated carbon production with a minimal formation of macropores that includes two stages: carbon heating up to 150–200°C in an oxygen atmosphere for 75 min and heating up to 750–900°C in a nitrogen flow for 15–45 min.

A new type of carbon has been developed specifically for natural gas storage at moderate pressures (2 MPa) [28]. The sorbent was prepared with the use of polyvinyldichloride, of which the cylinders were moulded, and next

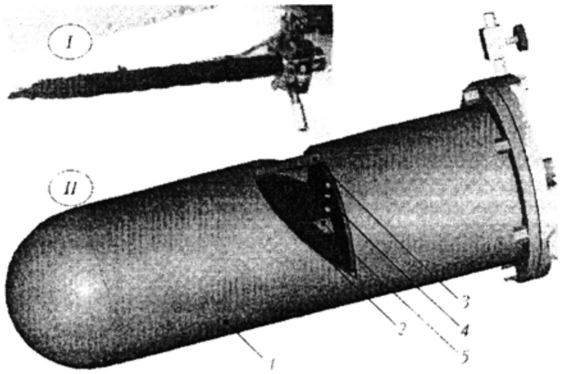


Fig. 2. Cylinder for adsorptive gas storage: I) photo of inner part of cylinder with sorbent: II) overall view of cylinder with cut (1) body; 2) sorbent; 3) perforated tube; 4) thermocouples; 5) heating element).

the process of pyrolysis was carried out. Such a material possesses a high specific surface and a large volume of micropores.

Despite the fact that more than 90 grades of activated carbon are produced in the USA, in 1995 at the University of Illinois a project was lauched [29] aimed at creation of highly efficient and cheap sorbents based on local coal with its subsequent physical and chemical activation for the purpose of natural gas storage.

In [30] a study is made of a new class of materials with a highly developed surface synthesized by processing of cheap natural clays by hydroxide of aluminum chloride or by zinc chloride solutions which could also be applied for methane storage.

Thus, there are strong grounds for assenting that for decades to come natural gas adsorbed in micropores of a solid sorbent will be an alternative to compressed gas.

We propose a vessel for natural gas storage in the adsorbed state (VGSAS) at a pressure of 3.5 MPa. The VGSAS represents a cylinder filled with a sorbent, which contains a gas in the adsorbed and compressed form. The free gas fills the macropores, while the adsorbed gas is held by the forces of molecular interaction mainly in the micropores, the size of which is comparable to the molecules adsorbed. Owing to the high pressure values within the adsorption space (60–80 MPa) the density of gas storage in the cylinder with the sorbent increases. To decrease the influence of heat of adsorption, a cylindrical finned heating element (HE) and three perforated tubes for radial feed of the gas are incorporated into the cylinder. The HE can be a heat pipe, a thermosiphon drain, a one-phase heat exchanger, or an electric heating element. In an effort to the develop sorption-based systems of gas storage, an investigation was made of methane adsorption by a sorbent based on activated carbon, i.e., carbon fiber "Busofit."

2. Experimental Setup for Determination of Methane Adsorption by Microporous Sorbents. To study methane sorption and to select a cylinder filler, we built an experimental setup that models the gas filling and bleed gas delivery at temperatures of from −40 to +40°C and at pressures of from 0.1 to 4 MPa (Fig. 1).

The processes of sorption were experimentally studied by the method of successive weight measurements. Important features of the gravimetric method are the fact that it does not need exact determination of the "parasitic" volume of the system and independence of the adsorption value at each point from the error of preceding measurements.

The main unit of the setup is a stainless vessel which models a real cylinder in a scale of 1:50 (Fig. 2). It has a length of 0.54 m and an inner diameter of 0.047 m. In the central part of the vessel, inside a stainless tube 10 mm in diameter, an electric heater 5 is mounted. A 12.5-mm-thick layer of sorbent 5 is wound on the tube (see Fig. 2, I). On the internal surface of the vessel body are three thin-walled stainless tubes 3 with holes over their entire lengths for free passage of the gas. Along the sorbent radius three Chromel–Alumel thermocouples 4 are placed with a spacing of 5 mm. On a flange, a valve, a pressure transducer, and a "mushroom" joint for input of the thermocouples into the vessel are mounted. Four thermocouples are embedded along the body of the experimental volume.

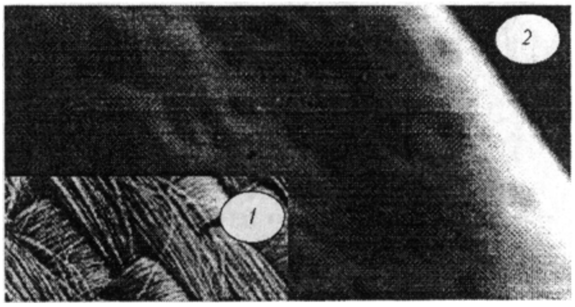


Fig. 3. Activated carbon fiber "Busofit AUTM-2": 1) cloth structure (×50); 2) porous fiber structure (×25,000).

TABLE 1. Equilibrium Adsorption Characteristics of Activated Carbon Fiber "Busofit" ($P = 3.5$ MPa, $T = 273$ K)

Carbon fiber	Sample	Adsorption value, a, kg/kg	Volume density of methane storage ρ, nm^3/m^3	Coefficients in the Dubinin–Radushkevich equation	
				a_0	D
"Busofit AUTM," felt	B1	0.113	80.7	0.12	$0.81 \cdot 10^{-6}/R^2$
"Busofit AUTM-2," cloth	B2	0.12	65.1	0.128	$1.82 \cdot 10^{-6}/R^2$
"Busofit TM," cloth multilayered	B3	0.135	94.5	0.144	$1.977 \cdot 10^{-6}/R^2$

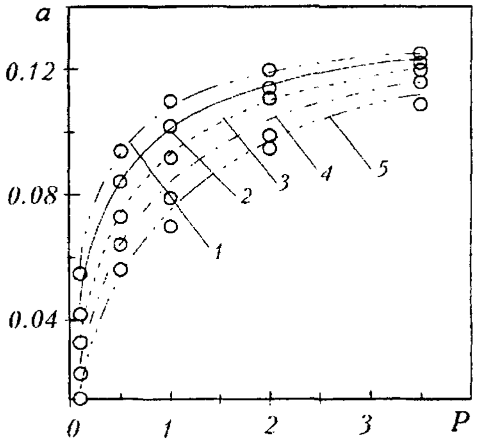
TABLE 2. Thermophysical and Structural Characteristics of Activated Carbon Fiber "Busofit"

Sample	ν, kg/m^3	S, m^2/g	V for mesopores (for benzene), cm^3/g	V for micropores (for benzene), cm^3/g	ε	C, J/(kg·K)	λ, W/(m·K)
B1	500	1400	0.15	0.4	0.39	1016	0.360
B2	380	1560	0.17	0.46	0.6	840	0.282
B3	490	1610	0.17	0.51	0.43	900	0.345

Prior to experiments the free volume of the vessel, including the total volume of the sorbent pores, was measured by means of helium. For this, the gas from helium cylinder 13 was fed via a pressure regulator 14 to a calibrated vessel 9. Thereafter, valve 18 was shut and valve 8 connecting the calibration space and experimental vessel 1 was opened (see Fig. 1). The differential pressure was determined from the readings of a transducer 10. The free volume was calculated by the Clapeyron–Mendeleev equation. In determining the amount of methane in the gaseous phase, the compressibility coefficient was assumed to be 0.94 for the pressure and temperature ranges investigated. After calibration, the helium was released via a safety valve 19 from the measuring system.

Prior to experiments the sorbent was subjected to prolonged evacuation by a vacuum pump 11 with simultaneous heating of the sorbent layer 24 by an electric heater 25 up to temperatures of 300–350°C. The process was controlled using the readings of thermocouples 23 arranged over the sorbent layer and on the surface of the experimental vessel and the readings of pressure transducer 10. Sorbent purification (regeneration) was considered to be complete if after closing the valve on the vacuum line 17, with a mean temperature of 300–350°C over the sorbent layer, the readings of the pressure transducer remained unchanged for 30 min.

To measure methane adsorption isotherms, a portion of methane was supplied from cylinder 12 to the experimental vessel via a pressure regulator 15 and a system of manual shut-off valves 8, 16, 18. The temperature in the safety chamber 3 was regulated by a heat exchanger 4 and a thermostat 5. Homogeneity of the temperature field inside the chamber was ensured by fans 22 and controlled in accordance with the readings of thermocouples 21. The problem was reduced to determination of adsorption by the gain in the adsorbent weight in relation to the pressure at a given temperature after establishing equilibrium. For weighing on an electronic balance 2, the experimental vessel 1 was disconnected from the gas main using valve 8. On completion of the experiment, the gas was disposed by means of a gas meter 20.



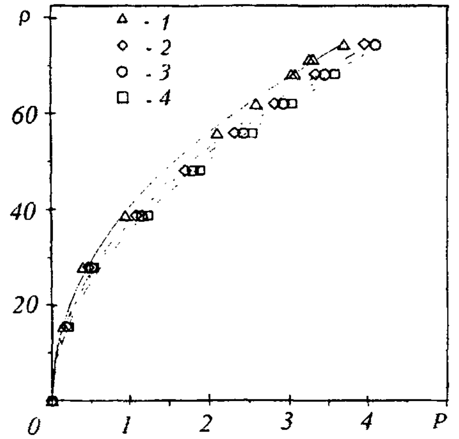


Fig. 4. Experimental (points) and calculated (curves) isotherms of methane adsorption on carbon fiber "Busofit AUTM-2": 1) $T = 233$ K; 2) 253; 3) 273; 4) 293; 5) 313.

Fig. 5. Volume density of methane storage vs. pressure in VGSAS at different temperatures: 1) $T = 293$ K; 2) 303; 3) 308; 4) 313.

In the course of the experiments, the readings of the electronic balance 2, thermocouples 21, 23, and pressure transducers 7, 10 were automatically recorded with the aid of a personal computer 6 using a program package in Delphi.

Results of the experimental study of the sorption and structural and thermophysical characteristics of the fibrous carboneous material "Busofit" of three grades (Fig. 3) produced at the Svetlogorsk association "Khimvolokno" (the Republic of Belarus) are given in Tables 1 and 2. "Busofit" is obtained by a technique of progressive activation of the products of cellulose fiber carbonization by steam with different scorchings at temperatures of from 850 to 1100°C. As is seen from the tables, the carbon fiber investigated refers to microporous sorbents with a developed surface and a complicated bimodal structure. It possesses a high methane adsorption capacity within the range of moderate pressures. Its adsorption value ranges from 0.113 to 0.135 kg/kg at a temperature of 0°C, which corresponds to activated carbon of the best grades used as fillers of cylinders for adsorptive gas storage [9, 10, 17, 31, 32].

As a result of the experiments, we obtained methane adsorption isotherms for carbon fiber "Busofit" of different grades and the empirical coefficients a_0 and D for the Dubinin–Radushkevich equation of isothermal adsorption

$$a = a_0 \exp \left(- D \left[RT \ln \left(\frac{P_s}{P} \right) \right]^2 \right) . \tag{1}$$

Equilibrium state equation (1) includes the saturation pressure P_s. Since the methane adsorption isotherms are measured within the temperature and pressure intervals comprising the regions of supercritical states of the adsorptive (T_c = 190.77 K, P_c = 4.626 MPa), the notion of saturation pressure loses its physical meaning. Two approaches are available to resolve this contradiction. The first consists in calculation of P_s by the Antonioni formula. In the second approach the saturation pressure is determined by the formula [33]

$$P_s = \left(\frac{T}{T_c} \right)^2 P_c . \tag{2}$$

A comparison of these two methods has shown that the use of Eq. (2) allows more accurate determination of the adsorption value.

Figure 4 gives, as an example, the adsorption isotherms for sample B2. The experimental data fit the calculated adsorption values with an error (up to 10%) sufficient for practical purposes.

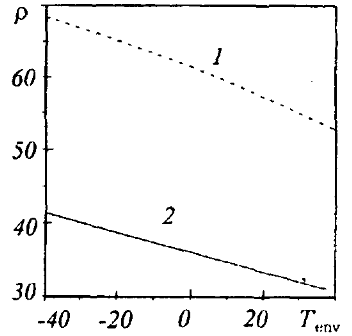


Fig. 6. Volume density of methane storage at charging pressure of 3.5 MPa in VGSAS (1) and in standard vessel with compressed gas (2) vs. ambient temperature.

In the experiments the total amount of methane was measured. Figure 5 illustrates the change in the volume density of methane storage in the course of VGSAS charging, which is accompanied by an increase in volume pressure of up to 4 MPa. In the general case, the volume density of gas storage is a function of the pressure and temperature and depends on the type of isothermal adsoption equation. It should be noted that in charging the gas cylinder the gas is absorbed by the sorbent due to the process of physical sorption. As a result of mutual attraction of the methane and the carbon fiber molecules, the concentration of a gaseous matter at the phase boundary becomes higher than in the gas phase. The methane is adsorbed by the microporous structure of the cylinder filler. Adsorption is a completely reversible process. On discharging the VGSAS, desorption occurs, i.e., gas molecules are removed from the sorbent.

Figure 6 provides data on charging the VGSAS and a standard gas cylinder in the winter and summer seasons. An analysis of the results shows that a cylinder filled with the carbon fiber "Busofit AUTM-2" is capable of providing a volume density of methane storage of 55–68 nm^3/m^3 within the temperature range of 273–313 K. This is severalfold higher as compared to the conventional method of natural gas storage in the compressed state.

CONCLUSION

1. With due regard for energetic, ecological, and economic problems natural gas of low and moderate pressures is a true alternative to conventional motor fuels.

2. The most promising method of creating vehicular reserves of natural gas is adsorption of the latter in a solid sorbent filling the cylinder. Activated carbons can be recommended as sorbents for adsorption systems. Theoretically, the maximum volume density of natural gas storage is 195 nm^3/m^3.

3. In the laboratory of porous media at the Academic Scientific Complex "Heat and Mass Transfer Institute" of the National Academy of Sciences of Belarus an experimental setup was created for investigation of solid-sorbent characteristics and reliable data have been obtained on methane sorption by carbon fiber "Busofit" of three grades at temperatures of from -40 to $+40^{\circ}C$ and at pressures of up to 4 MPa. The empirical coefficients in the Dubinin–Radushkevich equation of isothermal adsorption are determined.

4. A cylinder is developed that allows a decrease in the working pressure of from 20 to 3.5 MPa owing to the sorbent applied (carbon fiber "Busofit"), a decrease in the metal content of the structure, and an increase in the volume density of natural gas storage as compared to the conventional storage systems.

NOTATION

a, adsorption, kg/kg; a_0, D, coefficients in the Dubinin–Radushkevich equation; C, heat capacity, $J/(kg \cdot K)$; P, pressure, MPa; P_s, saturation pressure; P_c, critical pressure; R, universal gas constant, $J/(mole \cdot K)$; S, specific area, m^2/g; T, temperature, K; T_c, critical temperature; T_{env}, ambient temperature; V, specific volume, cm^3/g; ε, bed porosity; λ, effective thermal conductivity, $W/(m \cdot K)$; ρ, volume density of storage, nm^3/m^3; ν, bulk density, kg/m^3.

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