Thermally regulated cylinder for adsorption storage of a hydrogenous gas

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A B S T R A C T

A real alternative to a standard cylinder with compressed hydrogen or methane is the adsorption technology of a storing these gases at moderate pressures of 3.5–6 MPa. A thermally regulated heat pipe-based cylinder intended for onboard storage of a hydrogenous gas in an adsorbed form is described. A two-dimensional numerical model of heat and mass transfer and sorption processes in such a cylinder is suggested. The fins and heat pipe shell were used as part of the computational domain. Simulations of gas charging and discharging are performed using the commercial finite volume flow solver Fluent on ANSYS.

An experimental setup has been developed and data on the dynamic behavior of the carbon fibrous material-packed cylinder with hydrogen have been obtained and compared with calculations. The results of this work can be used in designing systems for adsorptive storage of hydrogen or methane that are of interest for power engineering, transport, and private usage.

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1. Introduction

Hydrogen and methane are universal heat carriers and energy accumulators. The main advantages of their application are due to their high caloric power, flexibility, and efficiency of the processes of energy transformation and the suitability for thermal engines without any substantial changes in their construction. Hydrogen and methane are capable of replacing any one of fuels in different branches of industry, power engineering, and transport. Hydrogen and methane do not contain toxic substances that are added, for example, to gasoline to raise its octane number. The unquestionable advantages of using hydrogen and methane is their ecological safety and the possibility of decreasing solid waste and harmful automobile ejections, as well as eliminating the greenhouse effect. One of the central problems in extensive application of a hydrogenous gas (hydrogen, methane, and their mixtures) is the high cost of their storage and transportation because of their low density in a gaseous state and low volumetric heat value. At atmospheric pressure and conventional temperature, 1 kg of hydrogen occupies a volume of 11 m^3. The high metal content of traditional vessels with a compressed gas, large energy expenditures on liquefaction of gas at cryogenic temperatures or its

compression up to 35–69 MPa, in combination with the negative effect on the properties of structural materials put the problem of developing the systems of rational storage of hydrogenous gas in the forefront and require the devising of new promising materials.

According to the standards [1] developed in different countries (Table 1), the present-day mobile system of hydrogen storage must have a storing capacity of 6–7 wt.% at mean pressures of 2–5 MPa and temperatures of 273–363 K, a holding capacity of 5 kg, and a specific energy of 7.2 MJ/kg. The Department of Energy of the USA has set an object of increasing the hydrogen storage capacity up to 9 wt.% by the year 2015 and shorten the time of charging to 2.5 min [2]. At the present time, there is no universal method of storing that would satisfy the above-formulated technical–operational requirements. The sorption technology of storing is closest to the practical realization of storage. This is the real alternative to compression up to high pressures or to gas liquefaction at low temperatures. The mass characteristics of such storage systems that exclude the possibility of explosion on leakage are comparable with high-pressure vessels and gradually approach on the average 6 wt.%. Such hydrogen adsorptive storage systems will find wide application in transport, power engineering (autonomous energy sources for decentralized use), as small-size power sources/accumulators of electronic devices (cellphones, portable computers, etc.).

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Nomenclature

a	current adsorption [kg/kg]	λ_{ef}	effective thermal conductivity of the sorbent bed [W/(m · K)]
a_{eq}	equilibrium adsorption [kg/kg]		
a^g	adsorbability [wt.%]	μ	dynamic viscosity [kg/(m · s)]
C	heat capacity [J/(kg · K)]	ρ_s	sorbent density [kg/m^3]
D_{s0}	phenomenological constant	ρ	sorbent bed density [kg/m^3]
E	activation energy [J/kg], sorption characteristic energy [J/kg]	ρ_g	gas density [kg/m^3]
		ρ^g	gravimetric storage density of gas in sorbent bed [wt.%]
E_g	total gas energy [J]	ρ^v	volumetric storage density of gas in sorbent bed [nm^3/m^3]
E_s	total energy of a solid sorbent [J]		
$\mathbf{F}$	force vector [N]	τ_{st}	stress tensor [Pa]
K	permeability [m^2]	τ	time [s]
$K_{s0} = 15D_{s0}/R_p^2$			
P	pressure [MPa]	*Subscripts*	
q_{st}	isosteric heat of adsorption [J/kg]	a	adsorbate
R_μ	gas constant [J/(kg · K)]	cr	critical
R_p	mean particle radius [m]	end	final value
S	spacing between fins [mm]	eq	equilibrium condition
T	temperature [K]	g	gas
$\mathbf{u}$	velocity vector [m/s]	hp	heat pipe
v_a	specific volume [m^3/kg]	s	sorbent
W_0	maximum specific volume of micropores [m^3/kg]	0	initial value
ε	sorbent bed porosity		

Noticeable advances have been made recently in the development of the systems of on-board storage of hydrogen, especially with the aid of carbon materials and metal hydrides. All the materials capable of storing bound hydrogen can be subdivided rather conventionally by the energy of binding an atom or a molecule of hydrogen with this material [2]. An important advantage of carbon sorbents is the decrease in energy expenditures on conducting desorption of gas molecules (to 2–4 ÷ 10 kJ/mole) as compared with metal hydrides (50–100 kJ/mole). The high specific surface and density, large volume of micropores, and the low cost are essential positive qualities of carbon sorbent-fillers of transport cylinders. The specific surface and specific capacity per unit volume and unit mass, the heat and kinetics of sorption can be related to the basic criteria with the aid of which one can preliminarily select porous materials that would be potentially promising for the systems of bound storage of gas. They determine such working parameters as the stock of gas, as well as duration of charging and discharging. Despite the different mechanisms of gas accumulation, the materials used as fillers in storage systems must conform to the requirements of economy, safety, and reliability; they must have an optimum mass for specific application; the capability for multiple charging and discharging. Often, as sorbents for gas storage, preference is given to activated carbons obtained as a result of thermal treatment of raw material (wood, saw dust, cellulose, peat, etc.) after impregnating them [3]. In Belarus, the carbon fibrous material "Busofit" is produced industrially in this way (the product of pyrolysis of impregnated cellulose). Such fibers can rather strongly hold molecules of both hydrogen and

methane because of the complex polymodal structure formed by the micropores, macropores, and mesopores and of the presence of a large number of defects.

The thermal effects of the processes of adsorption/desorption are closely related to the external heat transfer of the storage system, thermophysical properties of structural materials, and to the organization of heat transfer in the sorbent bed. The adsorption occurring in the course of cylinder charging with a hydrogenous gas is an exothermal process. An increase in the sorbent temperature, caused by release of the latent heat of phase transition and by the very low thermal conductivity equal to 0.1–0.4 W/(m · K), leads to a decrease in the quantity of gas stored under dynamic conditions as against the expected quantity. During discharging, the sorbent, on the contrary, is cooled additionally because of the endothermal character of desorption. This results in the formation of a unrecovered gas residue which decreases the efficiency of its usage. As follows from the investigations performed in [4–6], the temperature of the storing system is an important factor that determines the kinetics and thermodynamics of the processes of filling and extraction of gas. This causes the necessity of regulating the supplied and removed heat fluxes.

To make the sorption method of storing hydrogenous gas competitive, it is necessary not only to seek for new sorptive materials with improved properties, but also to design devices of thermal regulation capable of controlling the distribution and level of temperature in the sorbent bed and to influence the quantity of stored gas and the rate of its accumulation. The present paper considers the problems of development, experimental investigation, and

Table 1
Main requirements places upon the hydrogen storage system [1].

Parameters	Dept.of Energy of the USA (DOE)	Japan government program (WE-NET)	International Energy Agency (IEA)
Quantity of H$_2$, wt.%	>6	>3	>5
Density, kg/m^3	>45–60	–	–
Cost, US $/kg H$_2$	>40–130	–	–
Charging time, min	1–10	1–10	1–10
Temperature of H$_2$ desorption, K	273–363	374–423	353
Specific energy, MJ/kg	7.2	–	–
Cyclic stability	>90% after 5000 cycles		