INVESTIGATION OF THE SORPTION AND HEAT-EXCHANGE PROCESSES IN A HEAT PUMP WITH THE USE OF A THERMOSIPHON

L. L. Vasil'ev and L. E. Kanonchik

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A self-contained sorption heat pump of 2-kW power for heating and air conditioning is proposed. The nonequilibrium sorption and heat-exchange processes in a cylindrical adsorber with the use of a ribbed thermosiphon are described mathematically. The heat-engineering parameters of the structure are investigated.

Introduction. The traditional heat-and-cold systems are power-intensive and have a negative impact on the environment. The problem of decreasing the expenditure of primary energy is especially acute for decentralized consumers using hundreds of thousands of devices for heating and hot water supply — from individual stoves, systems of thermal treatment of milk, driers, and electric heaters to district boiler houses.

A rational solution of the above problems is the maximum use of natural gas and, as heating and air conditioning systems, heat pumps. According to the forecast of the world power committee, by 2020 75% of the heat supply in developed countries will be realized with their use.

At the present time, in industry, agriculture, and in the housing and public service sector worldwide 15 to 18 million heat pumps based on steam compression cycles with the use of freons are in operation, which considerably widens the possibilities of using low-potential energy due to its rational transformation. The increase in the low-potential heat temperature with the aid of heat pumps makes it possible to use "new" energy sources of natural (ambient air, ground waters, natural water reservoirs, solar energy) and technogenic origin (sewage works, industrial discharge channels, ventilation).

However, in accordance with the international Montreal protocol and Kyoto agreement, a commitment was made not to use freons — the cause of the appearance of the greenhouse effect in the terrestial atmosphere and destruction of the ozone protective layer of the atmosphere.

An alternative to the steam-compression freon heat pumps is sorption systems of obtaining heat and cold based on the thermodynamic desorption/sorption cycle. Gas heat pumps and refrigerators based on solid sorbents using electric energy or natural gas energy (gas burners) exhibit a unique ability to provide simultaneously conservation of primary energy for society and a decrease in the working costs for the final consumer. They can make a notable contribution to the solution of global ecological problems by refusing to use freons and changing to safe coolants. Adsorption heat pumps have no moving parts and make no noise or vibration. They are less sensitive to shaking and a change of position compared to absorption systems.

An adsorption refrigerator was first demonstrated by Faraday in 1848. Commercial use of sorption devices with silica gel [1] began in the 1920s. However, it was not before the 1980s that, under the influence of the energy and ecological crisis, sorption engineering began to be developed. The introduction of sorbents of a new type — synthetic zeolites and granulated activated carbons and composites based on them — made it possible to increase the efficiency of the sorption machines and widen the temperature range of their application.

In 1979, in the laboratories of the California Institute of Technology, works on the development of adsorption refrigerators were launched at the instruction of NASA. In ten years [2, 3], a number of reliable devices for space were developed, and in 1994 flight tests on the space shuttle were carried out as part of the Star Wars program. The high-efficiency cooling system of cryogenic infrared sensors incorporated compact compressors-adsorbers containing ammonia and carbon. The works of the Southern California gas company [4] proved the efficiency of using sorption

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technology in household refrigerators. In the USA, where cooling in the summer months and heating in the winter time are needed, a number of companies, such as "Wave Air Corporation," "SEMCO," and "Sharp," are actively developing heat pumps intended for year-round air conditioning in rooms [5, 6].

In Germany, gas sorption heat pumps based on zeolite and water, in which natural gas serves as a power supply and additional heat is taken from the ground, have found application. As a result, it is possible to obtain a heat power of 20 kW sorption with the assumption of 15 kW of heat from gas burning. In 1990, a 400-kW sorption heat pump was installed at a meat-packing plant [7]. Production of heat pumps based on solid sorbents of a power of 20 kW or more for conditioning systems was organized in Japan. Considerable efforts of researchers have been directed towards investigating the specific features of using chemisorption in high-temperature heat pumps [8]. In England and France [9–11], as in China [12–15], much consideration is given to their improvement by organizing effective heat and mass regeneration in adsorbers. In [12], a sorption heat pump with a cooling power of 4 kW and a transformation coefficient of 1.4 using plate-type ribbed heat exchangers and an activated carbon-methanol pair is presented. A new type of car air conditioner based on solid sorbents recovering the heat of exhaust gases is described in [12–15].

Sorption machines are an important element of modern energy-saving techniques, since their application widens the possibilities of making effective use of naturally scattered low-potential heat and reclaiming secondary energy resources of industrial production. This leads to a substantial saving of organic fuel and environmental protection from pollution. Sorption systems of obtaining heat and cold compete with steam-compression systems when the latter operate for a short time and use coolants with high coefficients of an adverse effect on the environment (a high greenhouse effect). In the last decade, the development and introduction of sorption machines was favored by the achievements in the field of heat regeneration and heat-transfer intensification [15–17] in a porous layer (inserts, ribs, heat pipes) and the organization of multi-stage cycles [18]. Of no small importance is the orientation to the employment in adsorbers of highly effective sorbing materials, such as compacted (briquetted) and monoclinic activated carbons [19–20] and metal chlorides [21]. The sorption technology can be more advantageous in the future in terms of economy, reduction of power consumption, and environmental protection.

Below we consider a 2-kW sorption ammonia heat pump with a self-contained power source — a cylinder for storing natural gas in the bound state at a low pressure (down to 4 MPa). As a sorbent in both the heat pump and the cylinder, the activated carbon fiber Busofit-AUTM is used. To analyze the influence of the operating conditions on the heat-technological characteristics of the structure, a two-dimensional model of nonequilibrium sorption and heat-exchange processes in the cylindrical layer of a sorbent with a ribbed thermosiphon is used.

Mathematical Modeling of the Nonequilibrium Problem. A number of authors [14, 16, 22, 23] note that in mathematical modeling it is necessary to take into account the fact that sorption is a nonequilibrium process and any final adsorption or desorption rate is associated with the temperature changes in the sorbent volume. A deviation from the equilibrium state of the sorption processes produces an effect on the characteristics of the sorption systems of obtaining heat or cold. Therefore, it is necessary to take into account the space-time distributions of the temperatures and concentrations in the sorbent layer.

The mathematical nonequilibrium model of the thermosiphon-based cylindrical adsorber (Fig. 1) is based on the following assumptions:

1) the pressure is constant throughout the sorbent layer with a high porosity and permeability;

2) the mass diffusion resistance is insignificant;

3) the adsorbent and adsorbate temperatures at each point are equal to one another because of the high values of the volume heat exchange between them;

4) in the sorbent layer, the deviation from the equilibrium state is defined by an approximate kinetics equation in which the motive force of the adsorption process is determined in terms of the adsorbate concentration difference in the solid phase.

With consideration for the assumptions made the model represents a system of equations — energy, kinetics, and equilibrium equations (equations of isothermal adsorption)

$$\rho_{s} \left(C_{ps} + aC_{pa} \right) \frac{\partial T_{s}}{\partial \tau} = \frac{1}{r} \frac{\partial}{\partial r} \left(r\lambda \frac{\partial T_{s}}{\partial r} \right) + \frac{\partial}{\partial z} \left(\lambda \frac{\partial T}{\partial z} \right) + q_{st} \rho_{s} \frac{\partial a}{\partial \tau}, \qquad (1)$$

$$\frac{da}{d\tau} = K_{\rm s0} \exp\left(-\frac{E}{R_{\rm \mu}T}\right) (a_{\rm eq} - a) , \qquad (2)$$

$$a_{\rm eq} = \left(\frac{W_0}{v}\right) \exp\left(-BT^2 \left[\ln\left(\frac{P_{\rm sat}}{P}\right)\right]^2\right),\tag{3}$$

where $K_{s0} = 15D_{s0}/R_p^2$, D_{s0} is a constant necessary for determining the surface diffusion coefficient, and R_p is the mean particle radius.

In the temperature range under investigation, the saturation curve $P_{sat} = P_{sat}(T)$ of the adsorbate is found by interpolating from the experimental data taken from the literature. The heat of the phase transition of sorption is calculated by the Clausius–Clapeyron equation with regard for the approximation of the vapor phase to the ideal state:

$$q_{\rm st} = R_{\mu} T \left[\frac{\partial \ln P}{\partial \ln T} \right] \Big|_{a=\rm const}.$$
(4)

For the isosteric heating/cooling stages during which the adsorber is closed, the additional mass condition is given in the form of the integral relation

$$\frac{d}{d\tau} \int_{\delta}^{S} \int_{r_0}^{r_1} a\left(T\left(r, z\right), P\right) r dr dz = 0.$$
(5)

In view of the expression for the adsorption rate this equation can be written in the form

$$\int_{\delta}^{S} \int_{r_0}^{r_1} K_{s0} \exp\left(-\frac{E}{R_{\mu}T}\right) (a_{eq} - a) r dr dz = 0.$$
(6)

When the adsorber is connected to the corresponding heat exchanger, for isobaric stages of desorption and adsorption the pressure is determined as

$$P(\tau, r, z) = P_{c} \quad \text{or} \quad P(\tau, r, z) = P_{e}. \tag{7}$$

Note that there is a direct analogy between the heat and mass exchange processes in the cylindrical vessel with adsorbed gas and in the heat pump adsorber [23–27]. In both cases, heating in the course of the desorption cycle and cooling at adsorption are necessary. At the same time, there are differences in the duration of the thermodynamic cycles and in the integral relation for the total mass of the adsorbate. For the systems of storing natural gas in the adsorbed state, this cycle is longer and the velocity of the gas flow from the vessel is fixed, and it is other than zero. What is more, the energy balance equation takes into account the radial component of the gas convection in the sorbent layer.

The solution of the system of equations (1)–(3) was obtained for the adsorber element containing inside a ribbed thermosiphon with the following initial and boundary conditions (Fig. 1):

$$T(r, z) |_{\tau=0} = T_0(r, z) = T_{\text{env}}, \quad P(r, z) |_{\tau=0} = P_0, \quad a(r, z) |_{\tau=0} = a_{\text{eq}}(T_0, P_0);$$
(8)

$$\frac{\partial T}{\partial z}\Big|_{z=0} = 0, \qquad \frac{\partial T}{\partial z}\Big|_{z=S} = 0, \quad -\lambda \frac{\partial T}{\partial r}\Big|_{r=R} = \alpha_{\rm env} \left(T - T_{\rm env}\right), \quad -\lambda \frac{\partial T}{\partial r}\Big|_{r=R_0} = \frac{Q_{\rm h}}{2\pi R_0 Sn}. \tag{9}$$

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Fig. 1. Calculated element of the cylindrical layer of the sorbent with a ribbed heater: 1) adsorber case; 2) rib; 3) sorbent; 4) heater (vapor-dynamic thermosiphon).

The method of finite-difference solution is based on the use of the standard finite-element [28] and matrix-run methods. The numerical solution of the nonequilibrium two-dimensional problem gives information on the dynamics of the processes and on the temperature and concentration fields and makes it possible to calculate the heat-technological characteristics of the heat-pump adsorber.

Description of the Machine. Figure 2 schematically represents the sorption heat pump for heating and conditioning with the following technical characteristics:

Heat-pump power at ambient temperature 278–293 K, kW	2
Heat-transformation coefficient	1.3–1.5
Power consumption, kW	1.33-1.55
Number of adsorbers	2
Weight, kg: sorbent	3
ammonia	3.6
Heat-exchange surface area of evaporator (condenser), m ²	1.6
Working pressure, MPa: evaporator	0.8
condenser	2.5

Continuity of operation of the sorption heat pump was provided by the presence of two identical antiphase loops (Fig. 2b). Each loop included a cylindrical adsorber 2.5 dm³ in volume, an ammonia collector 7, 7', a condenser, and an evaporator 5, 5'. As a housing material of the heat exchangers, black steel was used. The outer heat-exchange surface of the adsorbers was increased by welding to the housing of ribs of wire 2 mm in diameter.

The adsorber housings were filled with Busofit-AUTM compacted fibrous material. Activated carbon fiber of the Busofit type produced by the Svetlogorsk Production Association "Khimvolokno" (Belarus) is obtained by progressing activation by water vapors of carbonization products of cellulose fibers to different burns at temperatures between 850 and 1100° C. Among the advantages of the carbon fibrous sorbent are the high adsorption and desorption rates and various textile forms (in the form of cloth, braid, felt). This microporous sorbent exhibits unique physicochemical and mechanical properties and is compact (possibility of forming units). The adsorption and thermophysical properties of various brands of Busofit were determined on an ad hoc experimental facility [29]. The empirical coefficients in Eq. (3) for the Busofit-AUTM–ammonia pair have the following values: $W_0 = 0.491$ and $B = 1.61 \cdot 10^{-6}$. The investigation of the multicycle operation of the carbon fibers to reveal the possibility of their reuse has shown [30]



Fig. 2. Basic diagram of the heat pump based on solid sorbents: a) side view [1) adsorber; 2) thermosiphon; 3) condenser; 4) thermoelectric valve; 5) evaporator; 6) controlled throttle; 7) ammonia collector; 8) valve; 9) manometer; 10) steam pipeline; 11) liquid pipeline; 12) blower; 13) heating system (gas-flame path); 14) gas burner; 15) cylinder with adsorbed natural gas; 16) control unit]; b) top view [I) loop with adsorber 1; II) loop with adsorber 1'].

that the sorptivity of such a material after the first cycle changes and then stabilizes, reaching a certain stationary state. They can be regenerated as a result of thermal treatment and used repeatedly as a sorbent.

The vapor-dynamic, two-phase thermosiphons were chosen as heat-transfer devices for heating pieces of solid sorbent. They are characterized by the following features:

1) ability to transfer large heat flows at small temperature drops due to high values [31] of the heat-transfer coefficients of 10^3-10^5 W/(m·K);

2) possibility of providing fast heating of the sorbent in the adsorber under nonstationary conditions provided that the housing has a low heat capacity.

Vapor-dynamic thermosiphons are very flexible and convenient systems of thermal control. They are easy to mount inside the sorbent and have a small weight. To intensify the heat transfer in the sorbent layer and decrease the dimensions, steel ribs in the form of 0.8 mm-thick discs positioned on the thermosiphon condenser with a step of 6 mm and having a good contact with the housing were used.

Thermosiphons filled with water formed a part of the heating system, which came in two variants. For investigations and adjustment, electric ring heaters located in the evaporators of the thermosiphons were used. In the process of operation heat was supplied by a gas burner and a gas-flame path.

The condenser and the evaporator were made from pipes 5 mm in diameter combined by the collector. Development of the heat-exchanger surface from the air side was achieved by ribbing transverse to the wires on two sides. The ammonia collector was equipped with a porous insert from sintered nickel for more homogeneous evaporation in the sorption process. Heat removal into a heated room was realized due to the sequential blow of the adsorbers by VN-2 type blowers as well as by the natural convection from the condensers.

The main units of the heat pump were interconnected by a system of steam and liquid pipelines with blowers mounted on them. The integrity of the structure of the prototype of the heat pump was ensured by a framework from angles. After assembly the sorption heat pump was filled with ammonia. To intensity the heat exchange, the ammonia collector and evaporator unit was adjusted to function as a pulsating heat pipe. The throttle located at the condenser outlet decreased the pressure and temperature of the heat-transfer material.

The thermal system 13 was adjusted for alternate realization of the desorption process in each loop of the heat pump due to the continuous work of the heater (gas burner) and alternate switching of the thermoelectric valves 4 and 4' at intervals. Heating of adsorbers and cooling of condensers were realized during desorption. In the course of active operation of the adsorbers, i.e., when coolant vapors are being absorbed, they were cooled by means of corresponding blowers.

As a self-contained power source for the pump, a cylinder for sorption storage of natural gas served. The novel technology [26, 28] makes it possible to store natural gas in the sorbent-bound (activated carbon) state at a low pressure. The flat cylinder of the section type consisted of seven cylindrical sections enclosed in a flat thin-walled housing. Each section had a stainless steel case and was filled with a sorbent in which the gas was adsorbed in compressed form. To decrease the influence of the adsorption heat, a perforated pipe providing radial feed and extraction of gas was inserted into each section. The collector system of gas supply and removal combined individual perforated pipes and the pressure regulator regulating the total consumption. At a pressure of 3.5 MPa such a sorption system can provide a volume density of natural gas storage of up to 100 nm³/m³, which is 2–2.5 times higher as compared to the traditional cylinders with compressed gas.

Consider the operational procedure of this scheme of the heat pump under the conditions of continuous heat release. As mentioned above, this is achieved due to the antiphase operation of two loops and the continuous action of the gas burner 14. We start with the instant adsorption is taking place in the loop I adsorber (Fig. 2a) and the lowpotential heat from the environment (268-283 K) enters the evaporator 5 to cause ammonia evaporation at a lower pressure. Because of the diode effect, the ammonia vapors are transferred to the collector 7, where they condense. The phase transformation heat causes intensive evaporation of the liquid but already heated ammonia again. Ammonia vapors enter, through the pipeline, the absorber 1, where they are absorbed by the sorbent. The heat released during adsorption (exothermal process) is supplied, due to the thermal conduction of the ribs, to the outer surface of the adsorber and is removed by the blower 12. In so doing, the vapor-dynamic thermosiphon is not working, since the circulation of the heat-transfer material (water) in it is interrupted because of the application of voltage to the thermoelectric value 4. When the saturation of the sorbent reaches the given value, the adsorption process ceases and desorption begins. The air arrives at the gas-flame path, is mixed with the combustion products of the gas burner (the mixture temperature is 300-400°C), and blows the ring evaporator of the thermosiphon 2. In this period, the thermoelectric valve 4 and the blower 12 are off. As a result, the adsorber is heated by the external heat flow transferred by the thermosiphon condenser from the gas burner (or electric heater), the pressure in it increases, and the ammonia molecules are removed from the sorbent, i.e., the process of adsorption takes place. Then the hot ammonia vapors are driven off from the adsorber 1, pass through the valve 8, and condense on the walls of the condenser 3 cooled by natural air convection. The heat previously released in the adsorber is summed with the effective heat from the condenser; therefore, the heat-transformation coefficient of the cycle is always greater than 1. At the end of the desorption process the condensate is accumulated under the throttle 6 and is forced through it, having at the outlet a lower temperature and pressure. The liquid ammonia is drawn off into the collector 7 and the cycle is repeated. Thus, in adsorbers 1 and 1' the adsorption and desorption processes proceed alternately.

Results and Discussion. The numerical experiments modeled the real operational conditions of adsorbers as parts of the heat pump in the course of the thermodynamic cycle consisting of isobaric stages of desorption and adsorption and isosteric stages of heating and cooling. The calculations corresponded to the following data set: $T_{env} = 283$ K, the heat-exchange coefficient on the outer surface of the adsorber $\alpha_{env} = 3-10$ W/K·m², the heat flow from the external source $Q_h = 1.25$ kW. The steel housing of the adsorber had a length of 1.3 m, $R_0 = 0.02$ m, and a thickness of the walls of 0.001 m. The height of the ribs coincided with the layer thickness of the sorbent whose external radius was $r_1 = 0.3$ m.

As follows from Fig. 3, the combination of three characteristic temperatures (desorption, condensation, and evaporation temperatures) influences the processes of heat and mass exchange in the adsorber and determines the efficiency of the machine on the whole.

To estimate the efficiency of the sorption machines, the following parameters are used:



Fig. 3. Specific sorptive power of the adsorber with a ribbed thermosiphon for various condensation temperatures as a function of the temperatures of: a) desorption; b) evaporation [1) 313; 2) 323; 3) 333 K].



Fig. 4. Specific sorptive power of the absorber as a function of the ribbing height of the thermosiphon for various spacings: 1) 5; 2) 10; 3) 15 mm.

Fig. 5. Operational characteristics of the sorption machine with two loops: 1) heat power; 2) COP.

1) sorptive (cooling) power
$$Q_a = \left(M \int_{0}^{\tau_c} \frac{da}{d\tau} (r^*(T_c) + C_{pa}(T_d - T_c)) d\tau \right) / \tau_c$$
;

- 2) specific sorptive (cooling) power $Q_M = Q_a/M$;
- 3) heat power $Q_{h,p} = Q_a + Q_h$;
- 4) heat-transformation coefficient COP = $(Q_a \tau_c + Q_h \tau_d)/(Q_h \tau_d)$.

From Fig. 3a it is seen that a considerable enhancement of operational characteristics is observed at an optimum heating temperature of the sorbent and a lower condensation temperature. As the desorption temperature increases, the specific sorptive power gradually increases, reaches its maximum value, and then decreases. This is due to the simultaneous decrease in the duration of the cycle and in the amount of the adsorbate participating in it.

The results of the calculations (Fig. 3b) confirm that the increase in the evaporation temperature and the decrease in the condensation and evaporation temperature difference promote an increase in the specific sorptive power. The thermodynamic cycle becomes shorter, since less heat is supplied to the sorbent because of the specific features of the isotherms of ammonia sorption by the carbon fiber.

Figure 4 illustrates the influence of the height (sorbent-layer thickness) and the spacing between the ribs on the characteristics of the sorption machine. For example, when the ribbing height is increased from 20 to 60 mm at a fixed spacing of 2S = 5 mm, the specific sorptive power is continuously decreasing from 320 to 100 W/kg. With increasing sorbent-layer thickness the amount of the ammonia participating in the cycle grows to increase the sorptive power, but the sorbent mass, too, increases and the heat-transfer conditions deteriorate. According to the data obtained, the application of high widely spaced ribs produced a negative effect and their proper choice favors the intensification

of the heat exchange and equalization of the temperature in the sorbent layer. However, they occupy part of the effective volume of the cylinder.

The dynamics of change in the heat power and the heat-transformation coefficient of the sorption machine in the course of the working cycle is shown in Fig. 5. Note the mean value of the abstracted heat flow is close to 2 kW and the heat-transformation coefficient changes from 0.4 to 1.8. The duration of the working cycle of the two-loop heat pump is about 30 minutes.

CONCLUSIONS

1. For decentralized consumers, a 2-kW ecologically clean sorption heat pump with a self-contained power source — a cylinder for adsorption storage of natural gas — has been developed. The key element of both devices is a cylindrical vessel filled with Busofit-AUTM compacted carbon activated fiber.

2. On the basis of the two-dimensional nonequilibrium model of heat and mass exchange in the cylindrical sorbent layer a numerical analysis of the operating characteristics of the sorption heat pump has been performed. The results of the investigations have shown that the proposed heat pump provides a decrease in the primary energy cost due to the use of the low-potential energy of the ambient air (the mean heat-transformation coefficient is equal to 1.3-1.5), a specific sorptive power of up to 300 kW/kg, and a specific heat power of about 660 kW/kg.

NOTATION

a, current or nonequilibrium value of adsorption, kg/kg; *B* and W_0 , empirical coefficients; C_p , specific mass heat capacity, J/(kg·K); *E*, activation energy, J/kg; *H*, rib height, m, mm; K_{s0} , pre-exponential factor in the approximated kinetics equation; *M*, mass, kg; *n*, number of calculated cells in the adsorber; *P*, pressure, Pa; q_{st} , heat of the phase transition or isothermal heat of sorption, J/kg; Q_h , heat flow supplied to the sorbent from the external source, W; *r* and *z*, cylindrical coordinates, m; r^* , latent heat of vaporization, J/(kg·K); *R*, external radius of the absorber housing, m; R_0 , internal radius of the heating-element (thermosiphon) sheath, m; r_0 and t_1 , internal and external radii of the ring layer of the sorbent, m; R_{μ} , gas constant, J/(kg·K); 2*S*, ribbing spacing, m, mm; *T*, temperature, K, ^oC; *v*, specific volume, kg/m³; α , heat-transfer coefficient, W/(m²·K); 2 δ , rib thickness, m, mm; λ , effective heat capacity of the sorbent layer, W/(m·K); ρ , sorbent framework density, kg/m³; τ , time, sec; COP, heat-transformation coefficient. Subscripts: eq, equilibrium conditions; c, condensation; e, evaporation; d, desorption; env, environment; h, thermosiphon; h.p, heat pump; 0, initial value; a, adsorbate, adsorption; s, sorbent; sat, saturation; st, isosteric; p, particle.

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