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Limiting Efficiency of Adsorption Heat Pump

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Abstract—Based on the concept of unrecoverable energy losses in small-scale dissipative structures, the upper limit of the heat pump efficiency has been estimated. This limiting efficiency is achieved in the absence of energy losses due to heat exchange with the heat carrier but when nonequilibrium nonisothermal vapor transfer is taken into account. The limiting efficiency is smaller than the thermodynamically equilibrium efficiency and serves a better reference point in the search for optimal process layout.

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STATEMENT OF THE PROBLEM

Dissipative structures emerging in real dynamic systems are on such a small scale that it is impossible, in principle or for technical and economic reasons, to recover the energy dissipated in these structures. Hereinafter, such structures are referred to as dissipative structures with unrecoverable energy loss (DSUEs). DSUEs, as any dissipative structures, produce entropy in the system. In short-cycle adsorption systems for gas separation, the DSUE scale is the adsorption front extension [1]; and in energy installations with chemical oxidation of fuel, the DSUE scale is the size of the catalytic insert synchronizing the fuel oxidation rate and the expansion rate of a gas mixture in a turbine [2]. Taking into account the entropy production in DSUEs makes it possible to estimate the limiting efficiency, which, as distinct from the equilibrium efficiency, determines a more realistic upper limit for the efficiency of real systems. Let us illustrate this with the example of the adsorption heat pump. Figure 1 shows the principle scheme of heat flows in the adsorption heat pump. In the steady periodic regime, the device receives the heat Q_{hs} from a source with the temperature T_{hs} and the heat Q_{ev} from an evaporator with the temperature T_{ev} and loses the supplied heat Q_s to the environment with the temperature T_{env}. The efficiency of the working cycle of the adsorption heat pump is characterized by the coefficient of performance (COP) $\eta = Q_{ev}/Q_{hs}$, the ratio of the amount of produced cold to the amount of supplied heat [3]. For the equilibrium cycle, the efficiency (η_c) of the adsorption heat pump can be expressed through the above temperatures [3]:

$$\eta_c = \frac{Q_{ev}}{Q_{hs}} = \frac{T_{ev}}{T_{hs}}\frac{T_{hs}-T_{env}}{T_{env}-T_{ev}}. \qquad (1)$$

The typical cycle of the adsorption heat pump consists of two isobars (the adsorption and adsorbent regeneration stages) and two isosteres (the adsorbent heating and cooling stages) [3–7]. At the isobaric adsorption stage, the adsorber is connected through the gas phase with the evaporating compartment of a refrigerator where the constant temperature T_{ev} and the corresponding equilibrium pressure of the working fluid $p_{ev} = p(T_{ev})$ are maintained. At the isobaric regeneration stage, the adsorber is connected with a condenser where, during vapor condensation, the constant temperature T_c equal to the temperature of the environment ($T_c = T_{env}$) and the corresponding equilibrium vapor pressure $p_c = p(T_c)$ are maintained. For increasing the efficiency of the adsorption heat pump, it has been suggested to regenerate the adsorption heat [3, 4].

A heat pump with adsorption heat regeneration has two internal circulation loops (Fig. 2): the loop of the working fluid, through which the condensed working fluid returns to the evaporating chamber, and the heat carrier loop [6]. In the course of adsorption, the adsorbent is cooled with a heat carrier flow, which leads to an increase in the amount of the adsorbate. In the course of regeneration, the adsorbent is heated with a heat carrier flow, which leads to a decrease in the amount of the adsorbate. Calculations [4–7] and experiments [8, 9]

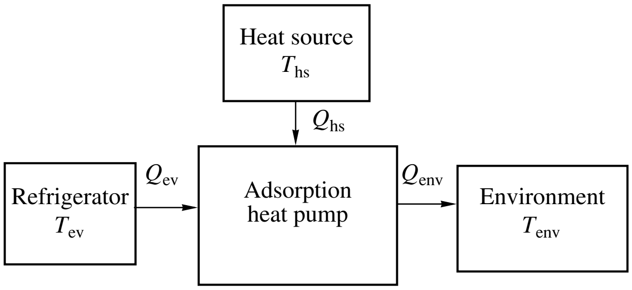

Fig. 1. Principle scheme of heat flows in the heat pump: the subscript indices hs, env, and ev denote the heat source (heating system), the environment, and the evaporator, respectively.

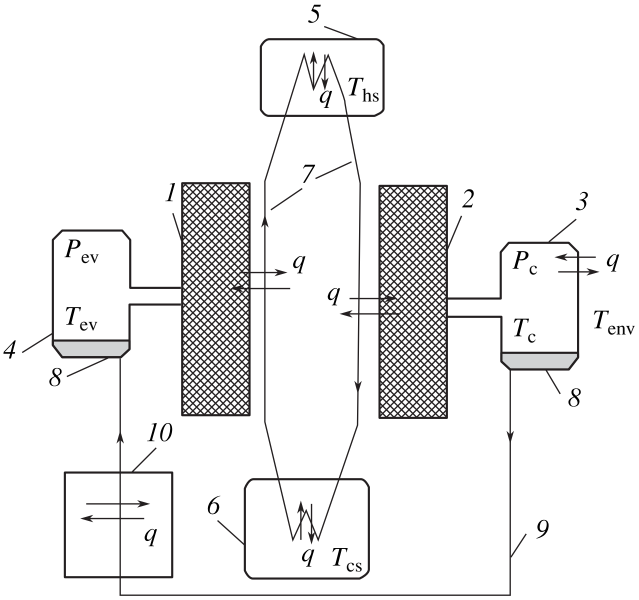

Fig. 2. Detailed layout of the heat pump: *1* and *2* are the adsorbers, *3* is the condenser, *4* is the evaporator, (*5*) is the heating system for the heat carrier, *6* is the cooling system (cs) for the heat carrier, *7* is the circulation loop of the heat carrier, *8* is the liquid (working fluid), *9* is the working fluid loop with refrigerator *10* ($T_{cs} = T_{env}$, q is heat exchange).

have shown that the equilibrium η_c value cannot be attained by optimizing the heat exchange processes in different elements of the heat pump. Heating and cooling of the adsorbent and heat carrier can be equilibrium. The losses due to cooling the working fluid in the evaporating chamber are negligible as compared to the heat of evaporation. Nevertheless, the considerable difference between the equilibrium efficiency and the experimental or theoretical efficiency is evidence that dissipative structures whose characteristic scale is much smaller than the size of heat-exchange devices are present in the working cycle of the heat pump. An important feature of the isobaric adsorption and regeneration stages is the constancy of the working fluid pressure in the adsorbent bed. When the heat pump has acceptable performance, the vapor flow becomes so strong that a thin temperature boundary layer is formed near the adsorbent (adsorption stage) or condensate (regeneration stage) phases. It is precisely these boundary layers that are responsible for the dissipative processes, and their scale prevents the recovery the energy dissipated in these processes. By analogy with [6], let us estimate the entropy production due to vapor transfer.

ENTROPY PRODUCTION AT THE STAGE OF ISOBARIC ADSORPTION

The adsorber is connected through the vapor phase to the evaporating chamber. In the evaporating chamber, *dm* moles of the working fluid, e.g., water, are evaporated under equilibrium conditions at the constant temperature T_{ev} and saturated vapor pressure p_{ev}. This vapor is heated in the adsorber under nonequilibrium conditions to the current temperature T of the adsorbent bed at the constant pressure p_{ev} and, then, is adsorbed under equilibrium conditions. The adsorbent bed at $T > T_{ev}$ delivers $c_p dm(T - T_{ev})$ joules of heat to the vapor. The entropy of the bed thereby decreases by

$$d_2 s = -c_p dm(T - T_{ev})/T,$$

whereas the entropy of the vapor increases by

$$d_1 s = c_p dm \ln(T/T_{ev}),$$

where c_p (J/(mol K)) is the molar heat capacity of the vapor. The total change in entropy upon transfer of *dm* moles of the vapor from the refrigerator to the adsorber can be presented as

$$d_a s = d_1 s + d_2 s = c_p dm\left[\frac{T_{ev}}{T} - \ln\frac{T_{ev}}{T} - 1\right]. \qquad (2)$$

If we introduce the quantity $q = (T - T_{ev})/T_{ev}$ and rewrite the expression in the brackets in Eq. (2) as a power series of q, it is easy to check that the inequality $d_a s > 0$ is valid. It is evident that, at the place where the vapor meets the adsorbent bed, there is an entropy source caused by a DSUE emerging due to nonequilibrium vapor heating. The differential *dm* can be expressed through the adsorption isobar differential $w(T)_{p = \mathrm{const}}$:

$$dm = m_0\left|\frac{dw}{dT}\right|_p dT, \qquad (3)$$

where w is the vapor adsorption in moles per unit mass of the dry adsorbent, m_0 is the mass of the dry adsorbent in the adsorber (the modulus symbol means that the adsorption amount decreases as the adsorbent temperature increases). In a stationary cycle, the adsorbate amount in the course of adsorption increases from $w_1 = w(p_{ev}, T_1)$ to $w_2 = w(p_{ev}, T_2)$. Thus, the initial (T_1) and final (T_2) temperatures of the bed at the adsorption stage ($T_2 < T_1$) can be calculated from the known adsorption isobar. Integrating Eq. (3) with taking into account Eq. (3), we obtain the total entropy production at the adsorption stage:

$$\Delta s_a = -c_p m_0 \int_{T_2}^{T_1} \frac{dw}{dT}\bigg|_{p = p_{ev}} \left[\frac{T_{ev}}{T} - \ln\frac{T_{ev}}{T} - 1\right] dT. \qquad (4)$$

ENTROPY PRODUCTION AT THE STAGE OF ISOBARIC REGENERATION

The adsorber is connected through the gas phase with the condenser. In the adsorber, *dm* moles of the working fluid are first desorbed under equilibrium conditions at the constant pressure p_c (equal to the pressure of the saturated working fluid vapor in the condenser) and the current temperature T of the adsorber and, then, are cooled under nonequilibrium conditions down to the temperature T_c. Then, the cooled vapor condenses at T_c under equilibrium conditions. On cooling, the vapor delivers $c_p dm(T - T_c)$ joules of heat to the condenser and its entropy decreases by $d_1 s = c_p dm \ln(T_c T)$, whereas the entropy of the condenser increases by $d_2 s = c_p dm(T - T_c)/T_c$. The total change in entropy at the desorption stage can be presented as

$$d_d s = d_1 s + d_2 s = c_p dm\left[\frac{T}{T_c} - \ln\frac{T}{T_c} - 1\right]. \tag{5}$$

If we introduce the quantity $g = (T - T_c)/T_c$ and rewrite the expression in the brackets in Eq. (5) as a power series of g, it is easy to check that the inequality $d_d s > 0$ is valid. This means that, at the inlet to the condenser, there is an entropy source caused by a DSUE emerging due to nonequilibrium vapor cooling.

In a stationary cycle, the adsorbate amount in the bed in the course of regeneration decreases from $w_2 = w(p_c, T_3)$ to $w_1 = w(p_c, T_4)$. The initial (T_3) and final (T_4) temperatures of the bed at the regeneration stage ($T_3 < T_4$) can be calculated from adsorption isobars. Integrating Eq. (5) with taking into account Eq. (3), we obtain the total entropy production at the regeneration stage:

$$\Delta s_d = -c_p m_0 \int_{T_3}^{T_4} \left.\frac{dw}{dT}\right|_{p = p_c}\left[\frac{T}{T_c} - \ln\frac{T}{T_c} - 1\right]dT. \tag{6}$$

Summation of Eqs. (4) and (6) gives the total entropy production in the stationary cycle of the heat pump with taking into account DSUEs ($\Delta S = \Delta S_a + \Delta S_d$). To simplify calculations, let us use integration by parts:

$$\Delta s = c_p m_0 \left\{ w_2\left[\left(\frac{T_{ev}}{T_2} - \ln\frac{T_{ev}}{T_2}\right) + \left(\frac{T_3}{T_c} - \ln\frac{T_3}{T_c}\right) - 2\right] \right.$$

$$- w_1\left[\left(\frac{T_{ev}}{T_1} - \ln\frac{T_{ev}}{T_1}\right) + \left(\frac{T_4}{T_c} - \ln\frac{T_4}{T_c}\right) - 2\right]$$

$$+ \int_{T_2}^{T_1} \frac{w(p_{ev}, T)}{T}\left(1 - \frac{T_{ev}}{T}\right)dT \tag{7}$$

$$\left. + \int_{T_3}^{T_4} \frac{w(p_c, T)}{T}\left(\frac{T}{T_c} - 1\right)dT \right\}.$$

It is worth noting that ΔS is independent of the heat source temperature T_{hs}.

EFFICIENCY OF THE CYCLE WITH DSUE

The entropy balance of the heat pump during one stationary cycle (Fig. 1) can be presented in the form

$$\frac{Q_{ev}}{T_{ev}} + \frac{Q_{hs}}{T_{hs}} + \Delta s = \frac{Q_{ev} + Q_{hs}}{T_c}. \tag{8}$$

The heat Q_{ev} removed from the refrigerator chamber can be presented as

$$Q_{ev} = Lm_0(w_2 - w_1) = Lm_0 Dw, \tag{9}$$

where L is the heat of evaporation of the working fluid (J/mol). Let us call the efficiency of the cycle with DSUEs (η_L) the limiting efficiency of the heat pump ($\eta_L = Q_{ev}/Q_{hs}$). It is evident that η_L is smaller than η_c since it takes into account the energy dissipated in DSUEs. Dividing both sides of Eq. (8) by Q_{ev}, we obtain the equation in the limiting efficiency:

$$\frac{1}{\eta_L} = \frac{1}{\eta_M} J_a \Delta S^* + \frac{1}{\eta_c}, \tag{10}$$

where $J_a = c_p T_c/L$ is the dimensionless Jacob number, $\Delta S^* = \Delta S/(m_0 c_p \Delta w)$ is the dimensionless entropy production per cycle, and $\eta_M = 1 - T_c/T_{hs}$ is the efficiency of a Carnot machine operating between thermostats with the temperatures T_{hs} and T_c. The η_L value is the upper limit of the efficiency of the heat pump in the absence of the heat transfer resistance in large-scale elements.

Example 1. Let us consider the adsorption heat pump with water and zeolite NaX as a working pair. This system has been studied theoretically [4–6] and experimentally [8]. The water adsorption on zeolite NaX was described in [8] by the modified Dubinin–Astakhov equation:

$$w = 0.261\exp\left\{-5.36\left(\frac{T}{T_s} - 1\right)^{1.73}\right\}, \tag{11}$$

where T_s is the temperature of the equilibrium liquid–vapor system ($T > T_s$).

As in the experimental work [8], we take t_{hs} = 200°C, t_{ev} = 7°C, and t_c = 40°C. At these temperatures, the thermodynamic efficiency of the equilibrium cycle (η_c) is 2.87 according to Eq. (1). The lower limit of the moisture content of zeolite (w_1) can be calculated by Eq. (11), using the temperatures of the heat source and condenser, i.e., at $T = T_{hs}$ and $T_s = T_c$. It turned out that w_1 = 0.0027 mol water/g. The highest moisture content (w_2) is taken to be 0.0086 mol water/g. Using Eq. (11), we can calculate the temperatures at the beginning and in the end of the isobaric stages of adsorption (T_1, T_2) and regeneration (T_3, T_4) corresponding to the specified adsorptions (w_1, w_2). These data are listed in Table 1. The solution of Eqs. (7) and (10) led to η_L = 2.33. This value is 25% lower than the η_c value corresponding to the thermodynamically equilibrium cycle. At the same

Table 1

	$w_1 = 0.0027$ mol/g	$w_2 = 0.0086$ mol/g
$t_{ev} = 7°C$	$T_1 = 423$ K	$T_2 = 353$ K
$t_c = 40°C$	$T_4 = 473$ K	$T_3 = 395$ K

Table 2

	$w_1 = 0.0068$ mol/g	$w_2 = 0.012$ mol/g
$t_{ev} = 10°C$	$T_1 = 335$ K	$T_2 = 318$ K
$t_c = 35°C$	$T_4 = 363$ K	$T_3 = 344$ K

time, η_L exceeds by a factor of 1.5 the maximal efficiency (1.6) calculated using the heat transfer equations in different elements of the heat pump [4] and by a factor of 3.5 the maximal experimental efficiency (0.6) [8].

Example 2. Let us consider the adsorption heat pump in which the working pair is water and a composite adsorbent composed of calcium chloride impregnated into a porous silica gel matrix. A series of such sorbents have been developed at the Institute of Catalysis, Siberian Division, RAS [10, 11]. Adsorption of water by these sorbents in wide ranges of water vapor temperatures and pressures was comprehensively studied by Aristov [12]. Processing the data from [12] by the least-squares method in the moisture content range 0.006–0.04 mol water/g, we obtain the asymptotic equation for water adsorption on the sorbent containing 33.7 wt % calcium chloride:

$$w = 0.0486\exp(-0.0003F). \tag{12}$$

Here, F is the Polanyi adsorption potential $\left(F = RT\ln\frac{p_s(T)}{p}\right)$, $R = 8.314 \times 10^{-3}$ kJ/(mol K) is the universal gas constant, $p_s(T)$ is the equilibrium vapor pressure at temperature T, and p is the vapor pressure in the adsorbent bed.

As in the experimental work [9], the heat source temperature is taken to be $t_{hs} = 90°C$, the temperature in the refrigerator is maintained at $t_{ev} = 10°C$ and that in the condenser, at $t_c = 35°C$. Substitution of these temperatures into Eq. (1) gives $\eta_c = 1.715$. The saturated water vapor pressures in the refrigerator (p_{ev}) and condenser (p_c) at the specified temperature, calculated by the Clausius–Clapeyron equation [13], turned out to be 12.1 and 54.2 mbar in the refrigerator and condenser, respectively. The lower limit of the zeolite moisture content (w_1) can be calculated by Eq. (12), using the vapor pressure in the condenser and the equilibrium water vapor pressure at the heat source temperature ($w_1 = 0.0068$ mol water/g). The maximal moisture content (w_2) is taken to be 0.012 mol water/g. The temperatures at the beginning and in the end of the isobaric adsorption (T_1, T_2) and regeneration (T_3, T_4) stages corresponding to the specified adsorptions w_1 and w_2 are calculated by Eq. (12) (Table 2).

The solution of Eqs. (7) and (10) allowed us to determine the limiting efficiency ($\eta_L = 1.52$). This value is 13% lower than the thermodynamically equilibrium efficiency η calculated by Eq. (1), but it exceeds by a factor of 2.5 the maximal experimental efficiency (0.6) [9]. The noticeable difference between η_L and the maximal efficiency calculated using the heat transfer equations or the experimental efficiency can be partially explained by heat losses due to heating followed by cooling the elements of the heat pump construction.

Thus, consideration of nonequilibrium associated with vapor transfer makes it possible to estimate the upper limit of the heat pump efficiency attainable in the absence of losses by heat exchange with the heat carrier. In the above examples, this limit considerably exceeds the experimental efficiency, thus confirming that there is considerable potential for improving performance of existing devices.

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