

Influence of desorption temperature on the thermodynamic performance of adsorption heat pump

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Abstract. In the paper an analysis of the desorption temperature effect on the thermodynamic efficiency of the adsorption heat pumps is presented. The thermodynamic performance of heat pump is determined by Coefficient of Performance (COP) as well as exergetic efficiency coefficient (η_{ex}) at the adsorption equilibrium conditions and compared to the performance at heat of evaporation of the working fluid conditions. Possible estimation of reduced efficiency of adsorption silica gel/water heat pump, as distinct from the equilibrium efficiency in realistic technical system is presented.

1 Introduction

In order to utilize the waste heat from industrial processes and low grade heat, such as solar energy or geothermal energy, adsorption systems are used in refrigeration and air conditioning systems as an alternative to vapor compression ones. Adsorption heat pumps utilize heat to drive thermodynamic cycles that transfer heat from a lower temperature to a higher temperature for applications such as space cooling and refrigeration or for improving energy efficiency of space heating or water heating even integrated with district heating network [1-3].

Activated carbon/methanol, activated carbon/ammonia, zeolite/water and silica gel/water are the adsorbent/adsorbate pairs commonly used in practical realised adsorption cycles. Adsorption heat pumps do not require moving parts for circulation of working fluid. They can work with low temperature driving energy sources, even it can be thermal energy storage. But they are characterised by many disadvantages such as low COP value, intermittently working principles, require advanced technology and special designs to maintain high vacuum [4-6].

The thermodynamic performance of heat pump is determined by COP as well as exergetic efficiency at the adsorption equilibrium conditions and compared to the performance at heat of evaporation of the working fluid conditions. Possible estimation of reduced efficiency of adsorption silica gel/water heat pump, as distinct from the equilibrium efficiency in practical technical system is presented.

2 Adsorption heat pump cycle

The operation of adsorption heat pumps is based on the ability of porous adsorbent to adsorb vapor

(adsorbate) at low temperature, and to desorb it when heated. The performance of an adsorption heat pump depends on many parameters, such as adsorbent and adsorbate properties, system design and operating conditions. The adsorption heat pump under consideration consists of an evaporator, an adsorber/desorber and a condenser (Fig. 1). The adsorber/desorber is encapsulated; it contains tubes with deposited adsorbent.

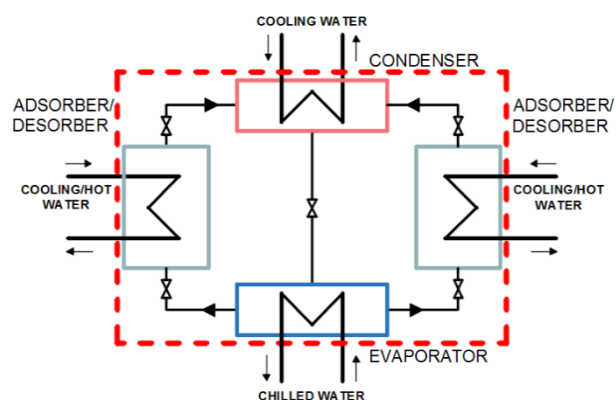


Fig. 1. Scheme of considered conventional single stage adsorption heat pump cycle.

The adsorption process is followed by preheating process to lift up the temperature and to lift up the pressure of the sorption reactor up to the condenser pressure. The desorption process starts afterward, then the temperature of sorption reactor approaches to the heat source temperature over time. Next precooling process starts, it cools down the adsorber/desorber to have low pressure equal to the evaporator pressure. When refrigerant from the evaporator is transported to the condenser and returns back to the evaporator then

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one cycle is completed and restarts circulation again [2, 7].

General equation of energy balance is written for all elements of the adsorption heat pump model:

$$\dot{Q}_{ac} = \dot{Q}_s - \dot{Q}_r + \dot{Q}_g \quad (1)$$

where \dot{Q}_{ac} is the heat flow accumulated in the process, \dot{Q}_s is the heat flow supplied to the process, \dot{Q}_g is the heat flow generated and \dot{Q}_r is the heat flow discharged from the process. Assessment of the exergy efficiency of the adsorption heat pump requires determining the organization of the adsorption cycle carried out in each of the absorbers included in its composition.

The operation mechanism of heat pump includes a number of cyclic transient processes. These processes run at different temperature and pressure levels in following stages. A simple adsorption cycle indicating all the heat transfer for a complete cycle is shown in Fig. 2.

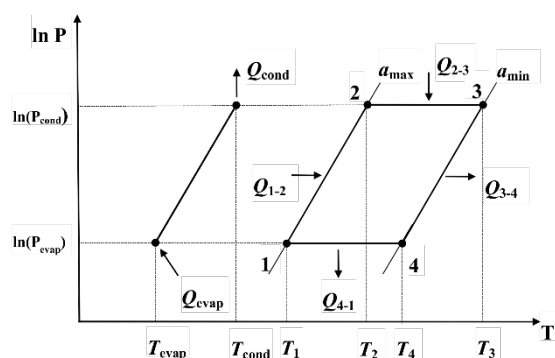


Fig. 2. Clapeyron diagram of the adsorption heat pump cycle.

(1-2) Isosteric heating of the saturated adsorbent along the isoster from temperature T_1 to the minimal desorption temperature T_2 . The temperature of adsorbent bed is increased from T_1 to T_2 by heating the adsorbent bed without desorption. The amount of heat, which should be transferred to the adsorbent bed from external source of temperature T_H is given by the relation:

$$Q_{1-2} = \int_{T_1}^{T_2} [m_a(c_{p,a} + a c_{p,v}) + m_t c_{p,t}] dT \quad (2)$$

(2-3) Isobaric desorption of the sorbate due to adsorbent heating from T_2 to the temperature $T_3 = T_{des}$, where T_{des} is the external heat source temperature. Subsequent condensation process in the condenser, where heat Q_{cond} is released to the outside of temperature T_{ot} . The pressure of the process remains constant. Part of the heat, which is transferred to the adsorbent bed, increases the temperature of adsorbate-adsorbent pair and adsorbent bed, while the other part causes the desorption process:

$$Q_{2-3} = \int_{T_2}^{T_3} [m_a(c_{p,a} + a c_{p,v}) + m_t c_{p,t}] dT + \int_2^3 m_a \Delta H_a da \quad (3)$$

(3-4) Isosteric cooling of the adsorbent along the isoster down from maximum temperature of the cycle T_3 to temperature T_4 . During this process, both the pressure and the temperature of the adsorbent bed decrease to the evaporator's values. Adsorbate concentration in adsorbent is constant. The amount of released heat is given by:

$$Q_{3-4} = \int_{T_3}^{T_4} [m_a(c_{p,a} + a c_{p,v}) + m_t c_{p,t}] dT \quad (4)$$

(4-1) Isobaric adsorption driven by adsorbent cooling down to $T_1 = T_{evap}$. Vaporisation of the adsorbate in the evaporator is started due to heat Q_{evap} transferred from external source of temperature T_L to the evaporator. Adsorbate concentration in adsorbent is increasing. During adsorbing of the adsorbate in the adsorbent heat is released due to heat of adsorption:

$$Q_{4-1} = \int_{T_4}^{T_1} [m_a(c_{p,a} + a c_{p,v}) + m_t c_{p,t}] dT + \int_4^1 m_a \Delta H_a da \quad (5)$$

The heat accumulated in the condenser can be determined based on the adsorbate mass desorbed by the adsorbent:

$$Q_{cond} = m_a \Delta a \Delta H_{evap} \quad (6)$$

where Q_{cond} is heat of condensation at the condenser temperature, and Δa is mass of adsorbate condensed at condenser. The amount of heat extracted in the evaporator Q_{evap} :

$$Q_{evap} = m_a \Delta a \Delta H_{evap} + \int_{T_{cond}}^{T_{evap}} m_a \Delta a c_{p,v} dT \quad (7)$$

where Q_{evap} is heat of evaporation and ΔH_{evap} is enthalpy of evaporation.

The heat of evaporation causes cooling effect, which can be used for cooling purposes. Heat of condensation can be employed for heating purposes.

The total amount of heat required to execute bed regeneration Q_{des} could be equal to heat supplied by the hot water from external heat source (generator) during the adsorbent regeneration (desorption) and affects the desorption of the adsorbate by increasing the temperature of the tube with the deposited adsorbent. Its value can be calculated from the following relationship:

$$Q_{des} = Q_{1-2} + Q_{2-3} \quad (8)$$

The total amount of heat released during stages 3 and 4 is:

$$Q_{ads} = Q_{3-4} + Q_{4-1} \quad (9)$$

3 Adsorption heat pump efficiency

Energy efficiency of adsorption heat pumps is reduced by thermodynamic losses due to the temperature differences between the cycle and ambient or external

sources. Designed temperatures of adsorption and desorption are the key factors of affecting efficiency.

The cooling effect in cycle occurs during the isobaric adsorption process (4-1) when the adsorbate is evaporated by gathering heat from external heat source (outside environment) [5, 8]. The heating effect appears during the isobaric desorption process (2-3) when the adsorbate is condensed by releasing heat to external source. In addition to the isobaric desorption process, the adsorbent bed is also cooled during (3-4) and (4-1) processes. The heat released during these processes can also be utilized for heating purposes in any process [6, 9].

In this paper thermodynamic analysis of an ideal cycle of single stage adsorption heat pump with reference to desorption temperature is performed. The efficiency of the working cycle is characterised by the Coefficient of Performance (COP), the ratio of the amount of produced cold (heat) to the amount of supplied heat [4, 6, 10]:

for cooling

$$\text{COP}_{\text{cool}} = \frac{Q_{\text{evap}}}{Q_{1-2} + Q_{2-3}} = \frac{Q_{\text{evap}}}{Q_{\text{des}}} \quad (10)$$

for heating

$$\text{COP}_{\text{heat}} = \frac{Q_{\text{cond}} + Q_{3-4} + Q_{4-1}}{Q_{1-2} + Q_{2-3}} = \frac{Q_{\text{cond}} + Q_{\text{ads}}}{Q_{\text{des}}} \quad (11)$$

For every heat pumping machine the maximal theoretical Coefficient of Performance is the Carnot COP [11-14]. In adsorption heat pumps, with assumption of reversibility of all processes and for the equilibrium cycle, the entropy generation is equal to zero $\Delta S = 0$ [15-17]. For an ideal cycle with assumption of zero thermal masses, during isobaric desorption $T_3 = T_{\text{des}}$ and during adsorption phase $T_1 = T_{\text{ads}}$, there is no temperature difference between the adsorber (or desorber) and the external heat source, so the entropy generation is zero, the energy balance (the first law) can be written:

$$Q_{\text{cond}} - Q_{\text{evap}} - Q_{\text{des}} + Q_{\text{ads}} = 0 \quad (12)$$

and the entropy balance (the second law):

$$-\frac{Q_{\text{cond}}}{T_{\text{cond}}} + \frac{Q_{\text{evap}}}{T_{\text{evap}}} + \frac{Q_{\text{des}}}{T_{\text{des}}} - \frac{Q_{\text{ads}}}{T_{\text{ads}}} = \Delta S \geq 0 \quad (13)$$

Then Carnot COP is based on the three temperature levels: evaporation temperature, desorption temperature and condensation temperature:

for cooling

$$\text{COP}_{\text{Carnot-cool}} = \frac{\left(\frac{1}{T_{\text{cond}}}\right) - \left(\frac{1}{T_{\text{des}}}\right)}{\left(\frac{1}{T_{\text{evap}}}\right) - \left(\frac{1}{T_{\text{cond}}}\right)} = \frac{\left(1 - \frac{T_{\text{cond}}}{T_{\text{des}}}\right)}{\left(\frac{T_{\text{cond}}}{T_{\text{ads}}}\right) - 1} \quad (14)$$

for heating

$$\text{COP}_{\text{Carnot-heat}} = 1 + \text{COP}_{\text{Carnot-cool}} = \frac{\left(\frac{1}{T_{\text{evap}}}\right) - \left(\frac{1}{T_{\text{des}}}\right)}{\left(\frac{1}{T_{\text{evap}}}\right) - \left(\frac{1}{T_{\text{cond}}}\right)} = 1 + \frac{\left(1 - \frac{T_{\text{cond}}}{T_{\text{des}}}\right)}{\left(\frac{T_{\text{cond}}}{T_{\text{ads}}}\right) - 1} \quad (15)$$

However experiments and calculations described by Zelenko, Heifets [18] and Sharonov, Aristov [19] proved that equilibrium $\text{COP}_{\text{Carnot}}$ cannot be achieved by the improving the heat exchange process in elements of the heat pump. The losses due to cooling the working fluid in the evaporator are negligible as compared to the heat of evaporation ΔH . Therefore Sharonov and Aristov [19] presented definition of COP for cooling and heating processes (below respectively) as ratio of enthalpy:

for cooling

$$\text{COP}_{\text{c-c cool}} = \frac{\Delta H_{\text{evap}}}{\Delta H_{\text{ads}}} \quad (16)$$

for heating

$$\text{COP}_{\text{c-c heat}} = 1 + \text{COP}_{\text{c-c cool}} = \frac{\Delta H_{\text{cond}} + \Delta H_{\text{ads}}}{\Delta H_{\text{ads}}} \quad (17)$$

where ΔH_{evap} is the enthalpy of evaporation, ΔH_{ads} is the average enthalpy of adsorption in the heat pump and ΔH_{cond} is enthalpy of condensation.

At temperatures along isobaric stages the entropy is generated due to the heat supply at $T_1 - T_{\text{ot}} > 0$ or the heat removal at $T_{\text{ot}} - T_{\text{cond}} > 0$, that reduces the cycle efficiency below the Carnot maximum values.

According to Clausius-Clapeyron equation for the gas pressure and assumption of Trouton's rule [19, 20] of intersection of adsorption isoster:

$$T_2 = \frac{T_{\text{cond}}^2}{T_{\text{evap}}} \quad (18)$$

relations (16-17) leads to relationships:

for cooling

$$\text{COP}_{\text{c-c cool}} = \frac{T_{\text{cond}}}{T_{\text{des}}} \quad (19)$$

for heating

$$\text{COP}_{\text{c-c heat}} = 1 + \frac{T_{\text{cond}}}{T_{\text{des}}} \quad (20)$$

There is degradation of efficiency due to entropy generation caused by external thermal coupling of the isothermal heat sources to the temperature varying adsorber, thus both $\text{COP}_{\text{c-c cool}}$ and $\text{COP}_{\text{c-c heat}}$ are always lower than Carnot COP.

The thermodynamic efficiency of adsorption heat pump is determined not only by Coefficient of Performance (COP) but also by thermodynamic (exergetic) efficiency coefficient (η_{ex}) [6, 11, 15] designated for the adsorption equilibrium conditions. The thermodynamic efficiency (exergetic efficiency) relates to actual performance of a system to its expected maximum performance as determined from ideal Carnot cycle and designated for the adsorption equilibrium conditions:

for cooling

$$\eta_{\text{ex-cool}} = \frac{\left(\frac{T_{\text{ot}}}{T_L} - 1\right) Q_{\text{evap}}}{\left(1 - \frac{T_{\text{ot}}}{T_H}\right) Q_{\text{des}}} \quad (21)$$

$$\eta_{\text{ex-cool}} = \frac{\text{COP}_{\text{cool}}}{\text{COP}_{\text{Carnot-cool}}} \quad (22)$$

for heating

$$\eta_{\text{ex-heat}} = \frac{\left(\frac{T_{\text{ot}}}{T_L} - 1\right)(Q_{\text{cond}} + Q_{\text{ads}})}{\left(1 - \frac{T_{\text{ot}}}{T_H}\right)Q_{\text{des}}} \quad (23)$$

$$\eta_{\text{ex-heat}} = \frac{\text{COP}_{\text{heat}}}{\text{COP}_{\text{Carnot-heat}}} \quad (24)$$

Compared to the reduced efficiency due to effect of enthalpy of evaporation, condensation and average enthalpy of adsorption, exergetic efficiency could be expressed by:

for cooling

$$\eta_{\text{ex-cool cc}} = \frac{\text{COP}_{\text{cool}}}{\text{COP}_{\text{c-c}}} \quad (25)$$

for heating

$$\eta_{\text{ex-heat cc}} = \frac{\text{COP}_{\text{heat}}}{\text{COP}_{\text{c-c}}} \quad (26)$$

Equations (25-26) represent possible estimation of reduced efficiency of adsorption silica gel/water heat pump, as distinct from the equilibrium efficiency in realistic technical system.

4 Results and conclusions

Using transient numerical model, developed and described in detail in previous Author's articles [21-23] to simulate silica gel/water adsorption heat pump system numerical analysis was done. The results of computer simulation were used to calculate the coefficient of performance for heating and cooling purposes.

To describe the adsorption characteristics the adsorption equilibrium equation (Dubinin-Astakhov) with appropriate coefficients was used (references [21-23]). Mathematical model is established comprising the set of heat and mass balance partial differential equations (PDEs), together with the initial and boundary conditions and is solved by the numerical method of lines (NMOL). The PDEs are reduced to a set of ordinary differential equations (ODEs) and is solved using Runge-Kutta 4th order numerical method. The main calculation element (adsorption/desorption column) contains three sub-elements that describe the component of the adsorber/desorber heat exchanger: heating/cooling water, metal pipe (tube of column), working bed (silica gel). For each calculation sub-element the heat and mass balance partial differential equations (PDEs) were formulated.

Performance is conducted for the two-bed adsorption heat pump (adsorber/desorber) with silica gel adsorbent and water as adsorbate. The adsorption equilibria of selected adsorbent-adsorbate pair was sourced from available literature [24-27]. Numerical simulation was conducted for Dubinin-Astakhov adsorption equilibria, for 1,5m length of sorption column, and temperatures $T_{\text{cond}} = 303 \text{ K}$, $T_{\text{evap}} = 283 \text{ K}$, $T_{\text{ads}} = 313 \text{ K}$. For the

calculation, more parameters that are necessary are according to paper [21]. Results of efficiency for cooling and heating purposes of silica gel/water adsorption heat pump in function of desorption temperature are presented in Figures 3-6 and Tables 1-4.

Table 1 and Fig. 3 shows the effect of desorption temperature on the COP coefficients including reduced COP for analysed adsorption heat pump in case of cooling applications. Maximum value of COP (Carnot) is presented as $\text{COP}_{\text{Carnot-cool}}$. As can be seen, the increase in desorption temperature slightly increases COP_{cool} , however it is lower than $\text{COP}_{\text{c-c cool}}$ due to cycle limitations of evaporation heat. Coefficient $\text{COP}_{\text{c-c cool}}$ estimates reduced efficiency of adsorption silica gel/water heat pump, as distinct from the equilibrium efficiency in practical technical system. Similar reduction in thermodynamic efficiency is presented in Table 2 and Fig. 4.

Table 1. Comparison of COP coefficients (for cooling).

T_{des} [K]	$\text{COP}_{\text{Carnot-cool}}$ [-]	$\text{COP}_{\text{c-c cool}}$ [-]	COP_{cool} [-]
343	1,65	0,88	0,071
353	2,00	0,86	0,154
358	2,17	0,85	0,179
363	2,34	0,83	0,198
368	2,50	0,82	0,211

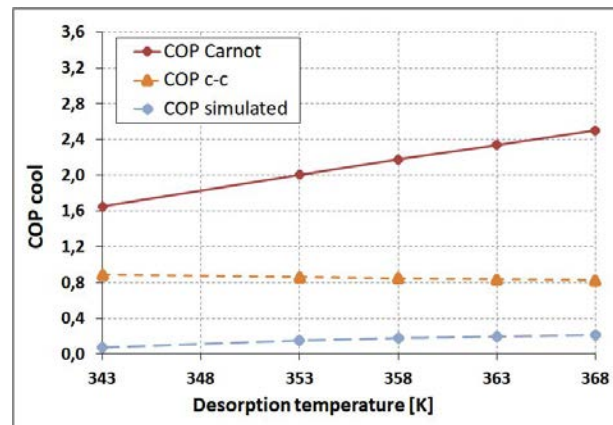


Fig. 3. Simulated COP (for cooling purposes) compare to reduced COP of silica gel/water adsorption heat pump in function of desorption temperature.

Table 2. Comparison of efficiency coefficients (for cooling).

T_{des} [K]	$\eta_{\text{ex-cool}}$ [-]	$\eta_{\text{ex-cool cc}}$ [-]
343	0,043	0,080
353	0,077	0,179
358	0,082	0,212
363	0,085	0,237
368	0,085	0,257

For heating applications of heat pump, comparison of COP coefficients in function of desorption temperature is shown in Table 3 and Fig. 5, and thermodynamic efficiency variation in Table 4 and Fig. 6. Carnot boundary value of COP is presented as $\text{COP}_{\text{Carnot-heat}}$.

The efficiency of heat pump is higher with lower temperature of the heat source as generator. Difference between basic COP and $COP_{c-c\text{ heat}}$ obtained according to limitations of heat of evaporation still indicates possibilities of improving efficiency in the realistic technical systems.

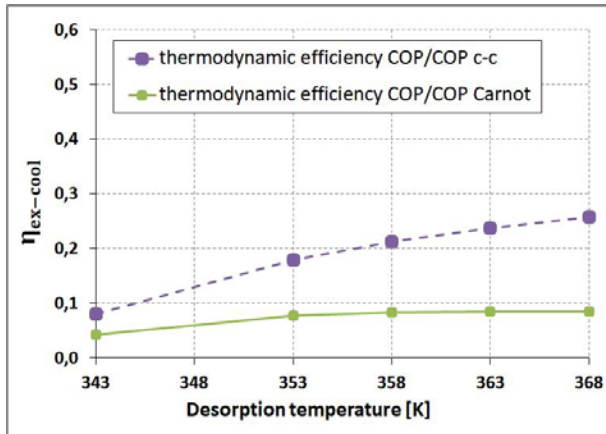


Fig. 4. Thermodynamic efficiency (for cooling purposes) of silica gel/water adsorption heat pump in function of desorption temperature.

Table 3. Comparison of COP coefficients (for heating).

T_{des} [K]	$COP_{Carnot-heat}$ [-]	$COP_{c-c\text{ heat}}$ [-]	COP_{heat} [-]
343	2,65	1,88	1,780
353	3,00	1,86	1,619
358	3,17	1,85	1,375
363	3,34	1,83	1,216
368	3,50	1,82	1,105

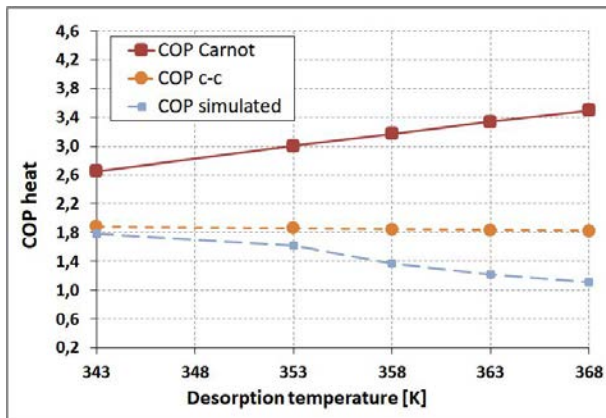


Fig. 5. Simulated COP (for heating purposes) compare to reduced COP of silica gel/water adsorption heat pump in function of desorption temperature.

Energy efficiency of adsorption heat pumps is reduced by thermodynamic losses due to the temperature differences between the cycle and ambient or external sources. Designed temperatures of adsorption and desorption are the key factors of affecting efficiency.

The considerable difference between the equilibrium efficiency and the theoretical efficiency is evidence that dissipative structure characteristic for the adsorption heat pump are present in the working cycle. Consideration of real nonequilibrium vapor heat transfer makes possible

to estimate the upper limit of the heat pump attainable with the heat of evaporation.

Moreover, efficiency of equilibrium in adsorption heat pump is always lower than the Carnot one due to the thermal entropy production caused by the external thermal coupling. Difference between basic COP and COP_{c-c} obtained according to limitations of heat of evaporation still indicates possibilities of improving efficiency in the realistic technical systems. The results presented in the cited articles [18-20] refer to various known working pairs as adsorbate and adsorbent, however for the silica gel/water working pair in the simulated adsorption heat pump performance is demonstrated in presented paper.

Coefficient COP_{c-c} estimates reduced efficiency of adsorption silica gel/water heat pump, as distinct from the equilibrium efficiency in practical technical system. This limit considerably exceeds the simulated efficiency, thus confirming that there is potential for improving performance of adsorption heat pumps in technical systems.

Table 4. Comparison of efficiency coefficients (for heating).

T_{des} [K]	$\eta_{ex-heat}$ [-]	$\eta_{ex-heat\ cc}$ [-]
343	0,672	0,945
353	0,539	0,871
358	0,433	0,745
363	0,364	0,663
368	0,316	0,606

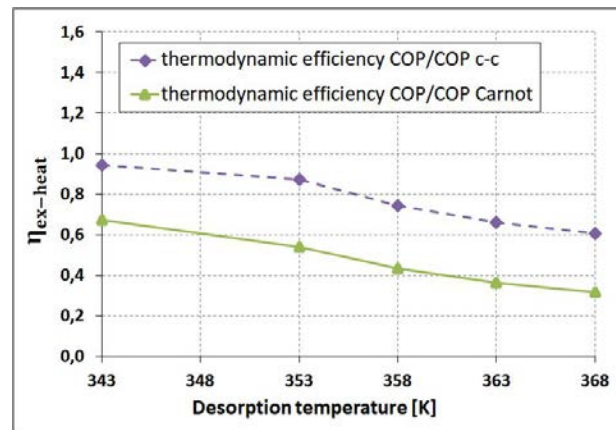


Fig. 6. Thermodynamic efficiency (for heating purposes) of silica gel/water adsorption heat pump in function of desorption temperature.

The COP and thermodynamic efficiency η_{ex} depend on generation (desorption) temperature T_{des} . It is connected with mass of generated adsorbate, thus with type of used adsorbent/adsorbate pair and its characteristic heat of evaporation.

In the application of analysed silica gel/water adsorption heat pump for refrigeration/cooling processes, the COP and efficiency slightly increases with increasing desorption temperature.

For heating purposes, when the interest is in utilising low grade heat sources, with analysed silica gel as adsorbent and water as working fluid and with

characteristic evaporation heat, the efficiency of heat pump is higher with lower temperature of the heat source as generator.

It can be observed that chosen silica gel/water working pair generates higher efficiency for heating than cooling utilisation of heat pump. Therefore, the type of adsorbent/adsorbate pair for the purpose of adsorption heat pump should be adapted. Some pairs will contribute to greater efficiency in refrigeration applications and other in heating applications.

Nomenclature

a - mass/amount adsorbed/desorbed on adsorbent at time τ , [kg kg⁻¹] (uptake)
 c_p - specific heat, [J kg⁻¹ K⁻¹]
 Ex - exergy (heat exergy) [kJ kg⁻¹]
 ΔH_a - isosteric heat of adsorption, [J mol⁻¹]
 Ex - exergy (heat exergy) [kJ kg⁻¹]
 ΔH - enthalpy of evaporation, [kJ kg⁻¹]
 m - mass/amount, [kg mol⁻¹]
 p - pressure [Pa]
 Q - heat, [J]
 \dot{Q} - heat flow, [W]
 S - entropy [kJ kg⁻¹ K⁻¹]
 T - temperature, [K]
 P - pressure, [Pa]

Greek letters

η - efficiency [-]

Subscripts

a - adsorbent
 ads - adsorption
 cc - refers to ratio of enthalpy
 $cond$ - condenser
 $cool$ - cooling
 des - desorption
 ex - exergetic
 $evap$ - evaporator
 f - fluid (water)
 $heat$ - heating
 H - high (warm source)
 L - low (cold source)
 ot - surrounding/environment
 t - tube/pipe
 v - adsorbate (water vapor)

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