

Modeling the performance of water-zeolite 13X adsorption heat pump

KINGA KOWALSKA*
BOGDAN AMBROŹEK

West Pomeranian University of Technology, Szczecin, Institute of Chemical Engineering and Environmental Protection Processes, al. Piastów 42, 71-065 Szczecin, Poland

Abstract The dynamic performance of cylindrical double-tube adsorption heat pump is numerically analysed using a non-equilibrium model, which takes into account both heat and mass transfer processes. The model includes conservation equations for: heat transfer in heating/cooling fluids, heat transfer in the metal tube, and heat and mass transfer in the adsorbent. The mathematical model is numerically solved using the method of lines. Numerical simulations are performed for the system water-zeolite 13X, chosen as the working pair. The effect of the evaporator and condenser temperatures on the adsorption and desorption kinetics is examined. The results of the numerical investigation show that both of these parameters have a significant effect on the adsorption heat pump performance. Based on computer simulation results, the values of the coefficients of performance for heating and cooling are calculated. The results show that adsorption heat pumps have relatively low efficiency compared to other heat pumps. The value of the coefficient of performance for heating is higher than for cooling

Keywords: Desorption; Adsorption; Mathematical simulation; Heat pump; Coefficient of performance

Nomenclature

A	–	adsorption potential, J/mol
E_0	–	characteristic energy of the adsorbent, J/mol
COP	–	coefficient of performance
COP_h	–	coefficient of performance for heating

*Corresponding Author. Email kingateresakowalska@gmail.com

COP_{ref}	–	coefficient of performance for cooling
C_{pa}	–	heat capacity of liquid adsorbate, J/(mol K)
C_{pf}	–	specific heat of fluid, J/(kg K)
C_{ps}	–	heat capacity of adsorbent, J/(kg K)
C_{pw}	–	specific heat of the wall, J/(kg K)
D_s	–	surface diffusivity, m ² /s
D_1	–	inner diameter of the heat transfer tube, m
D_2	–	outer diameter of the heat transfer tube, m
D_3	–	outer diameter of the adsorbent layer, m
h_f	–	heat transfer coefficient between the fluids and the tube, W/(m ² K)
h_s	–	heat transfer coefficient between the metal and the adsorbent, W/(m ² K)
ΔH_a	–	heat of adsorption, J/mol
ΔH_v	–	heat of vaporization, J/mol
L	–	length of the adsorbent layer, m
n	–	constant in the Dubinin-Astakhov equation
m_a	–	mass of adsorbent, kg
m_w	–	mass of metal tube, kg
p	–	vapor pressure of adsorbate, Pa
p_c	–	pressure of condensation, Pa
p_e	–	pressure of evaporation, Pa
p_s	–	saturation vapor pressure of adsorbate, Pa
q^*	–	equilibrium value of \bar{q} , mol/kg
\bar{q}	–	adsorbate concentration in adsorbent particle, mol/kg
Q_c	–	heat released in the condenser, J
Q_e	–	heat absorbed in the evaporator, J
Q_{1-2}	–	heat of isosteric heating process, J
Q_{2-3}	–	heat of isobaric desorption process, J
Q_{3-4}	–	heat of isosteric cooling process, J
Q_{4-1}	–	heat of isobaric adsorption process, J
r_p	–	radius of the adsorbent particle, m
R	–	gas constant, J/molK
t	–	time, s
T	–	temperature, K
T_a	–	temperature of adsorption, K
T_c	–	condenser temperature, K
T_{CO}	–	inlet temperature of cooling fluid, K
T_e	–	evaporator temperature, K
T_f	–	fluid temperature, K
T_H	–	inlet temperature of heating fluid, K
T_s	–	adsorbent temperature, K
T_w	–	wall temperature, K
T_1-T_4	–	initial temperature for heating, desorption, cooling and adsorption steps, respectively, K
v_f	–	fluid velocity, m/s
V	–	volume adsorbed, m ³ /kg
V_0	–	limiting adsorption volume, m ³ /kg
z	–	axial coordinate, m

Greek symbols

β	–	affinity coefficient
δ_w	–	thickness of the wall (heat transfer tube, inner tube thickness), m
δ_s	–	thickness of the adsorbent layer, m
ε	–	porosity of the adsorbent bed
$\rho(T)$	–	temperature dependent density of liquid adsorbate, mol/m ³
ρ_w	–	wall (heat transfer tube) density, kg/ m ³
ρ_f	–	fluid density, kg/m ³
ρ_s	–	adsorbent particle density, kg/m ³

1 Introduction

The recent years of civilization development have significantly influenced natural environment. Pollution generated by power plants and other industries has caused ecosystem degradation and created the need to replace conventional fuels with renewable sources. One of the technologies that delivers ‘clean energy’ is the adsorption heat pump. This systems has recently become an interesting field of research. The advantage of such a solution is the ability to use working pairs, which are fully environment-friendly and are characterized by simple working principles and long life time [1–9]. Moreover, the most important reasons for the use of adsorption heat pumps are simplicity, no moving parts, low maintenance requirements, and shock resistance. Due to this fact, adsorption heating devices can be used where large amounts of waste heat are generated, e.g., in chemical plants and power plants. Another application is for domestic purpose but it is still in phase of research and development.

The design of an adsorption heat pumps requires the knowledge of the thermodynamics and principle of working of these systems. In the adsorption heat pumps, transfer of mass and heat is a cyclic process. The efficiency of the heat pump depends on the appropriate selection of adsorbate-adsorbent pair, system design and temperature conditions. The adsorbate-adsorbent pairs should be characterized by high sorption capacities and the ability to work in a wide temperature range [1–3].

In this paper, a mathematical model of the cylindrical double-tube adsorption heat pump has been developed, taking into account heat balance equations for fluid, adsorbent wall, and adsorbent. The adsorption rate was calculated using a linear driving force (LDF) model. The method of the lines (MOL) was used to solve the mathematical model. As the working pair the system water-zeolit 13X was chosen. The results of computer simulations were used for analysis of the impact of evaporator and con-

denser temperatures on adsorption and desorption kinetics. The values of the coefficients of performance for heating and cooling were calculated. The problems encountered during the study were explained in the conclusions.

2 Adsorption heat pump description

An adsorption heat pump consists of four main parts: adsorber, condenser, evaporator, and the expansion valve. Figure 1 illustrates a schematic diagram of adsorption heat pump.

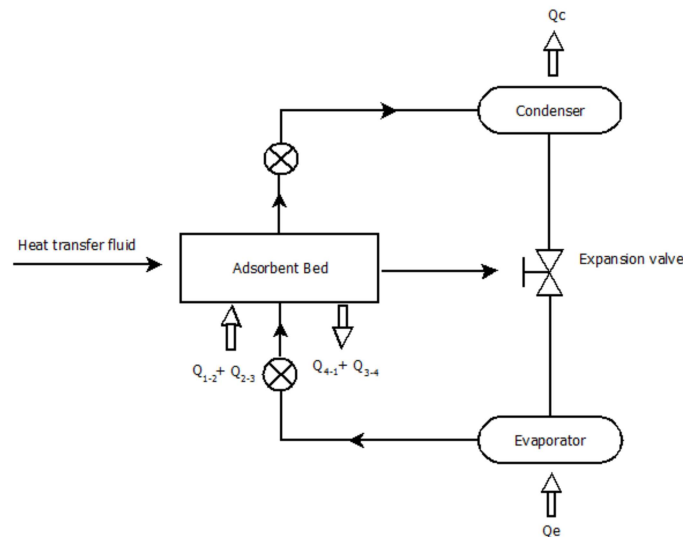


Figure 1: Schematic diagram of adsorption heat pump.

The adsorber is a cylindrical double-tube heated or cooled by an external fluid (Fig. 2). The inner tube is covered with adsorbent layer, e.g., zeolite surrounded by the outer tube to give space for working fluid vapor passage. The adsorbent may be in the form of: (1) grain or pellets (traditional adsorbent used as it is received from manufacturer), (2) powder consolidated by a binder or (3) powder consolidated by a binder and adhered on metal [2]. The first configuration is characterized by low heat transfer coefficient at metal–adsorbent interface, because of weak contact between the metal surface and adsorbent grains. Using consolidated adsorbents adhered on metal allows improvement of metal–adsorbent heat transfer due to adsorbent adhesion on metal surface.

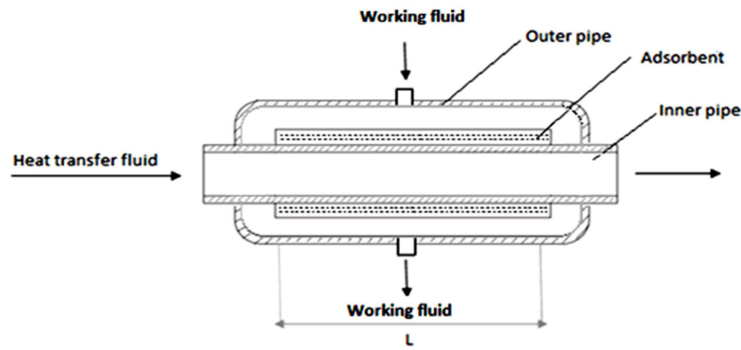


Figure 2: Schematic of the adsorber.

In adsorption heat pump adsorbate is circulated between adsorber, condenser, and evaporator. The thermodynamic cycle on an isoster of an adsorbent-adsorbate pair is presented in Fig. 3. Basically, an adsorption cycle consists of four steps: isosteric heating (1-2), isobaric desorption (2-3), and isosteric cooling (3-4), isobaric adsorption (4-1) [3].

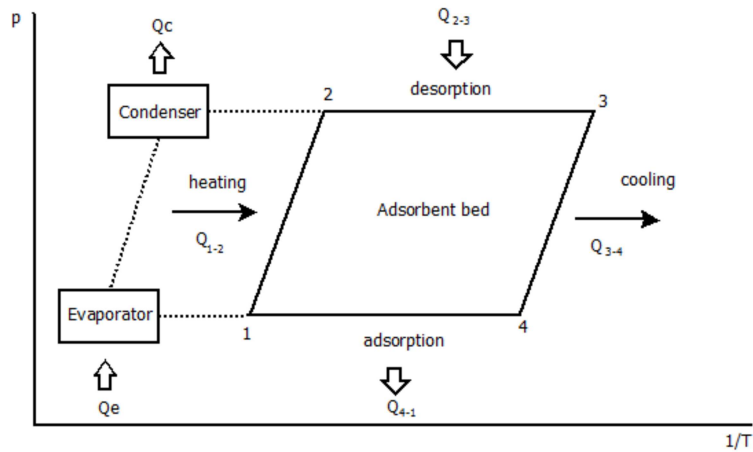


Figure 3: Adsorption heat pump cycle.

During isosteric heating (step 1-2) the adsorbent bed is heated by heat transfer fluid (HTF). The pressure increases from p_e to p_c due to working fluid vapor desorption. When the vapor pressure is equal to the condens-

ing pressure isobaric desorption begins (step 2-3). The adsorbent bed is connected to the condenser. The heat of condensation, Q_c , of the working fluid can be discharged into the environment or used for heating purposes. The liquid working fluid flowing from the condenser through the expansion valve is directed to the evaporator. At the end of desorption step adsorber is disconnected from the condenser and isosteric cooling starts (step 3-4). During this step, the bed is cooled using the heat transfer fluid. The pressure in the adsorbent bed decreases from p_c to p_e as a result of the lowering of adsorbent temperature and the adsorption of working fluid vapor. During adsorption (step 4-1) the bed is connected to the evaporator. This allows adsorption of working fluid vapors. Adsorbate is evaporated gaining heat from the environment, Q_e . In this way, the cooling effect occurs during the adsorption step. Adsorption is an exothermic process. Heat released during this process, Q_{4-1} , can be utilized for heating purposes. For this application, the heat removed from the adsorbent bed during cooling step, Q_{3-4} , can be also used [3].

Exhaust gas or oil can be used as a heat transfer fluid during heating and desorption. During cooling and adsorption, air and water are commonly used as a heat transfer fluid. For the water-zeolite system, the heat transfer fluid temperature during heating and desorption is in the range from 369 K to 633 K [3]. Evaporator and condenser temperatures for this system are included in the range from 275 K to 313 K and 293 K to 313 K, respectively.

3 Mathematical model of adsorption heat pump

The mathematical model describing the dynamic performance of adsorption heat pump consists of integrated partial differential and algebraic equations. A one-dimensional non-equilibrium model has been used. The model equations are obtained by applying differential energy and material balances to the control volume shown in Fig. 4.

The following assumptions are made:

- gas phase follows the ideal gas law,
- the pressure gradient across the bed is neglected,
- heat losses from adsorber to the ambient are negligible,
- solid and gaseous phases are in thermal equilibrium,

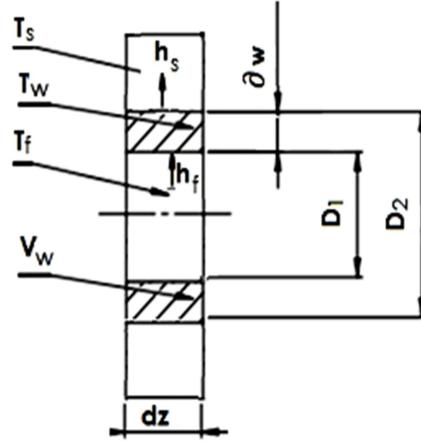


Figure 4: Control volume dz . T_s – adsorbent temperature, T_w – wall temperature, T_f – fluid temperature, V_w – volume of wall, h_s – heat transfer coefficient between the metal and the adsorbent, h_f – heat transfer coefficient between the fluids and the tube, D_1 – inner diameter of the heat transfer tube, D_2 – outer diameter of the heat transfer tube.

- radial concentration, temperature and velocity gradient within the adsorbent bed are negligible,
- intraparticle heat transfer resistance is negligible,
- adsorbent bed is consolidated by a binder and adhered on a metal surface,
- axial conduction within the column wall is negligible.

Based on the above assumptions, the energy balance for the heat transfer fluid is represented by the following equation:

$$v_f \frac{\partial T_f}{\partial z} + \frac{\partial T_f}{\partial t} = \frac{4h_f}{C_{pf}\rho_f D_1} (T_w - T_f) . \quad (1)$$

The energy balance for the inner tube is stated as

$$\frac{\partial T_w}{\partial t} = \frac{2}{\delta_w(D_2 + D_1)\rho_w C_{pw}} \left[h_f D_1 (T_f - T_w) - h_s D_2 (T_w - T_s) \right] . \quad (2)$$

The heat balance for the adsorbent bed can be written as

$$\frac{\partial T_s}{\partial t} - \frac{\Delta H_a}{(C_{ps} + \bar{q}C_{pa})} \frac{\partial \bar{q}}{\partial t} = \frac{2h_s D_2}{\delta_s (D_3 + D_2) \rho_s (1 - \varepsilon) (C_{ps} + \bar{q}C_{pa})} (T_w - T_s) . \quad (3)$$

Due to the fact that in the balance equations there is a component determining the mass transfer rate, it is necessary to determine a kinetic model. The mass-transfer rate inside the adsorbent particle is explained by the linear driving-force (LDF) model:

$$\frac{\partial \bar{q}}{\partial t} = \frac{15D_s}{r_p^2}(q^* - \bar{q}) . \quad (4)$$

The LDF model is a compromise between solution accuracy and calculation efficiency, and is adequate in most adsorption applications [10–15].

The boundary conditions for the HTF are:

Adsorption:

$$T_f|_{z=0} = T_{CO} , \quad (5)$$

$$\frac{\partial T_f}{\partial z}|_{z=L} = 0 . \quad (6)$$

Desorption:

$$T_f|_{z=0} = T_H , \quad (7)$$

$$\frac{\partial T_f}{\partial z}|_{z=L} = 0 . \quad (8)$$

The initial conditions for $0 < z < L$ and $t = 0$ are:

$$\bar{q}(0, z) = \bar{q}_0(z) ; T_s(0, z) = T_{s0}(z) ; T_f(0, z) = T_{f0}(z) ; T_w(0, z) = T_{w0}(z) . \quad (9)$$

The solution of the model equations requires the knowledge of the state of the adsorbent bed at the beginning of each step. In this paper, it is assumed that the final concentration of working fluid in adsorbent layer and temperature profiles in the adsorber for each step define the initial conditions for the next one. For the adsorption step in the first adsorption cycle:

$$\bar{q}_0(z) = 0 ; T_{s0}(z) = T_{f0}(z) = T_{w0}(z) = T_a . \quad (10)$$

The set of partial differential equations (PDEs) representing the adsorption heat pump (1)–(4), together with the boundary and initial conditions, (5)–(10), is solved by the numerical method of lines.

The spatial discretization is performed using second-order central differences with 10 equally spaced axial nodes, and the PDEs are reduced to a set of ordinary differential equations (ODEs). The set of ODEs is solved using the Polymath ODE Solver [16].

In order to calculate the coefficient of the performance of adsorption

heat pump, the following equations are used [3,4]:
isosteric heating (1-2)

$$Q_{1-2} = \int_{T_1}^{T_2} [m_a (C_{p,s} + \bar{q}C_{p,a}) + m_w C_{p,w}] dT, \quad (11)$$

isobaric desorption (2-3)

$$Q_{2-3} = \int_{T_2}^{T_3} [m_a (C_{p,s} + \bar{q}C_{p,a}) + m_w C_{p,w}] dT + \int_2^3 m_a \Delta H_a dq, \quad (12)$$

isosteric cooling (3-4)

$$Q_{3-4} = \int_{T_3}^{T_4} [m_a (C_{p,s} + \bar{q}C_{p,a}) + m_w C_{p,w}] dT, \quad (13)$$

isobaric adsorption (4-1)

$$Q_{4-1} = \int_{T_4}^{T_1} [m_a (C_{p,s} + \bar{q}C_{p,a}) + m_w C_{p,w}] dT + \int_4^1 m_a \Delta H_a dq, \quad (14)$$

the heat of evaporation

$$Q_e = m_a \Delta q \Delta H_V + \int_{T_c}^{T_e} m_a \Delta q C_{p,a} dT, \quad (15)$$

the heat of condensation

$$Q_c = m_a \Delta q \Delta H_V. \quad (16)$$

4 Selection of adsorbent-adsorbate pair

The performance of adsorption heat pump generally depends on the equilibrium and thermodynamic properties of the adsorbent-adsorbate working pair. For this reason the optimal working pair should be chosen individually for each configuration of heat pump. The design and dynamic simulation of these systems requires the knowledge of the adsorption equilibria for the system of interest, over a wide range of operation temperature and pressure. This information is used to calculate the heat of adsorption, which is crucial for the choice of working pair [17–23]. The results of extensive studies on the adsorption equilibrium for various adsorbate–adsorbent systems have been reported in [4]. These studies were done for the following adsorbate–adsorbent systems: water–alumina, water–silica gel, water–zeolite 13X,

ammonia-activated carbon, ammonia-charcoal, ammonia-polymer resin. Based on the information provided in this paper, water was selected as adsorbate, and zeolite 13 X as adsorbent. For the application being investigated, water has the following positive attributes: has a high latent heat of vaporization, is easily accessible, non-flammable and non-toxic. Adsorption isotherm of water on zeolite 13X has extremely non-linear pressure dependence, which is of importance in adsorption heat pump applications. The physical properties of zeolite 13X are given in article [4].

Adsorption equilibrium of water on zeolite 13X was described using the Dubinin-Astakhov (D-A) model:

$$V = V_o \exp \left[- \left(\frac{A}{\beta E_o} \right)^n \right], \quad (17)$$

where

$$A = RT \ln \left(\frac{p_s}{p} \right) \quad (18)$$

is an adsorption potential.

Values of D-A model are [4]: $V_o = 2.114 \times 10^{-4} \text{ m}^3/\text{kg}$, $\beta E_o = 18445.0 \text{ J/mol}$; $n = 1.806$. Equation (17) relates volume of adsorbed compound, V , partial pressure of adsorbate, p , and temperature, T . The concentration of adsorbate in adsorbent, q^* , is given by

$$q^* = V\rho(T) . \quad (19)$$

Saturation vapor pressure, p_s , and temperature dependent density of liquid adsorbate, $\rho(T)$, are calculated using the following relations:

$$\log_{10}(p_s) = D + E/T + F \log_{10}(T) + GT + HT^2 , \quad (20)$$

$$\rho(T) = BC^{-(1-T/T_c)^m} . \quad (21)$$

The values of the parameters are: $B = 347.10 \text{ kg/m}^3$, $C = 0.27400$, $m = 0.28571$, $T_c = 647.13 \text{ K}$, $D = 29.8605$, $E = -3.1522 \times 10^3$, $F = -7.3037$; $G = 2.4247 \times 10^{-9}$, $H = 1.8090 \times 10^{-6}$.

The isosteric heat of adsorption, (ΔH_a) , was determined from the equilibrium information using the Clausius-Clapeyron equation:

$$\Delta H_a = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_{q^*} . \quad (22)$$

For the calculation of the pressure derivative in the above equation, the relationship between pressure and temperature was described using D-A model (Eqs. (17)–(19)).

5 Results

A series of studies was carried out and the results of numerical simulations were presented in Figs. 5–8. The input values of heat pump parameters are collected in Tab. 1.

Table 1: Model input data.

Symbol	Value	Unit
C_{pw}	478	J/(kg K)
D_1	1.0×10^{-2}	m
D_2	1.2×10^{-2}	m
D_3	2.8×10^{-2}	m
$\frac{15D_s}{r_p^2}$	1.0×10^{-2}	1/s
h_f	1000	W/(m ² K)
h_s	250	W/(m ² K)
L	0.1	m
v_f	0.1	m/s
ε	0.65	–
ρ_s	2280	kg/m ³
ρ_w	7800	kg/m ³

Figure 5 shows the variations of the cooling fluid, the wall and the adsorbent bed temperatures at two different positions during adsorption process. These results are obtained for the initially clean bed. As can be seen, adsorption is a highly exothermic process.

The effect of the evaporator temperature on the adsorption kinetics is shown in Fig. 6. As can be seen, the increase in evaporator temperature increases the amount of adsorbed working medium. This is obvious because as the evaporator temperature increases, the vapor pressure of the working medium increases as well.

Figure 7 shows the changes in temperatures of the solid phase, column walls and fluid at two different positions. It can be seen that all these temperatures are practically the same after about 250 s. The influence of the condenser temperature on the desorption kinetics and on the final concentration of the adsorbate in the adsorbent bed is shown in Fig. 8. It can be observed that as the temperature of the condenser increases, the final

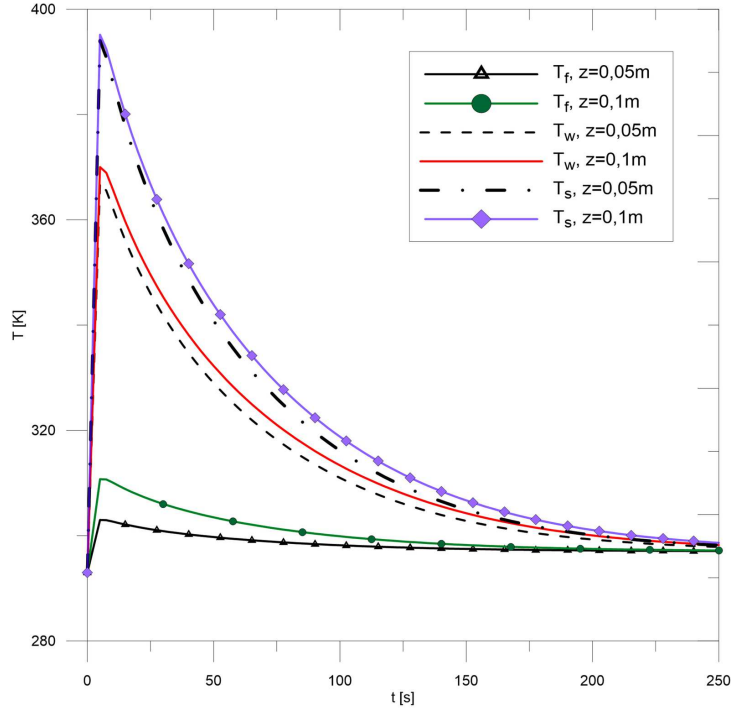


Figure 5: Time evolutions of the cooling fluid, the wall and the bed temperatures at two different positions during adsorption process ($T_a = 293$ K, $T_e = 273.5$ K, $T_{CO} = 293$ K).

content of the adsorbate in the bed increases as well.

The results of the computer simulations were used to calculate the coefficient of performance for heating and cooling (COP_h and COP_{ref} , respectively). These coefficients are defined as follows:

$$COP_h = \frac{Q_c + Q_{3-4} + Q_{4-1}}{Q_{1-2} + Q_{2-3}}, \quad (23)$$

$$COP_{ref} = \frac{Q_e}{Q_{1-2} + Q_{2-3}}. \quad (24)$$

Exemplary calculation results are shown in Tab. 2. As can be seen, the value of the coefficient of performance for heating is higher than for cooling.

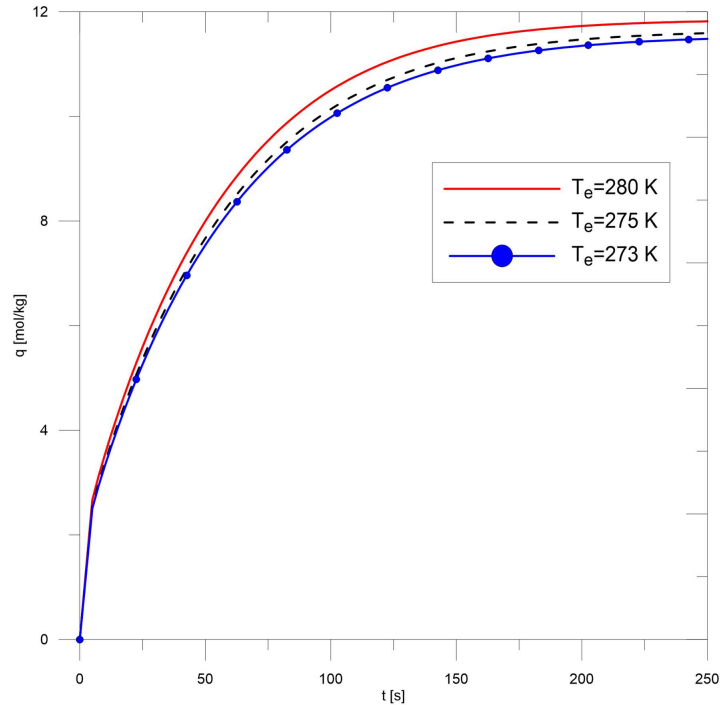


Figure 6: The effect of evaporator temperature on the adsorbate concentration in adsorbent bed during adsorption process ($z = 0.05$ m, $T_a = 293$ K, $T_{CO} = 293$ K).

Table 2: Coefficients of performance of cylindrical double-tube adsorption heat pump for heating and cooling ($T_H = 533$ K, $T_{CO} = 293$ K, $T_e = 273.5$ K, $T_c = 313$ K).

COP_{ref} [%]	COP_h [%]
32	54

6 Conclusions

In this paper, a nonequilibrium model has been developed and used for predicting the dynamic performance of cylindrical double-tube adsorption heat pump. The model is based on the energy and mass conservation laws, stated in one-dimensional form and solved in time and space using the method of lines. Linear driving-force (LDF) model was used to calculate the mass transfer rate. Water was selected as adsorbate, and zeolite

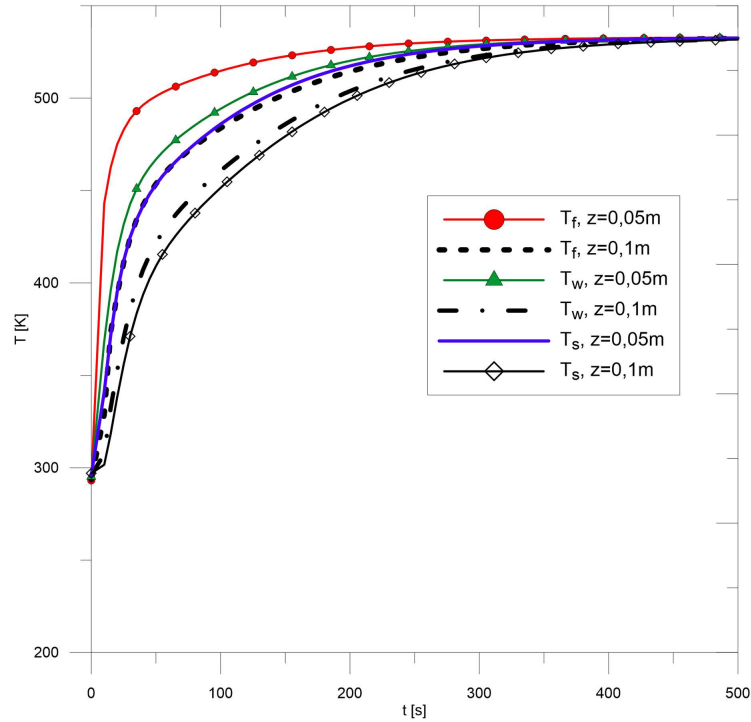


Figure 7: Time evolutions of the heating fluid, the wall and the bed temperatures at two different positions during desorption process ($\bar{q}_0(z) = 11.37 \frac{\text{mol}}{\text{kg}}$, $T_{s0}(z) = T_{f0}(z) = T_{w0}(z) = 293 \text{ K}$, $T_c = 313 \text{ K}$, $T_H = 533 \text{ K}$).

13 X as adsorbent. Adsorption equilibrium was described using the Dubinin – Astakhov (D-A) model. The effect of the evaporator and condenser temperatures on the adsorption and desorption kinetics, respectively, was examined.

The results of the computer simulations allowed the calculation of the coefficient of performance (COP) for heating (COP_h) and cooling (COP_{ref}). Obtained value of $COP_{ref} = 32\%$ and $COP_h = 54\%$ showed that the adsorption heat pumps have relatively low efficiency compared to other heat pumps. For this reason, installations of this type are best suited for waste heat.

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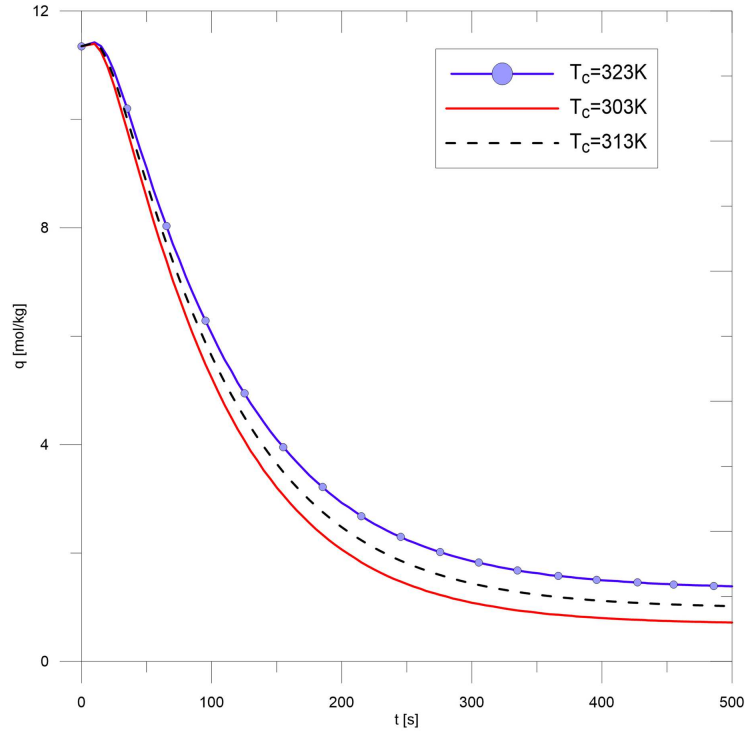


Figure 8: The effect of condensation temperature on the adsorbate concentration in adsorbent bed during desorption process ($z = 0.05$ m, $\bar{q}_0(z) = 11.37 \frac{\text{mol}}{\text{kg}}$, $T_{s0}(z) = T_{f0}(z) = T_{w0}(z) = 293$ K, $T_H = 533$ K).

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