MONIKA GWADERA, KRZYSZTOF KUPIEC, JAN RAKOCZY*

INVESTIGATION OF THERMAL EFFECTS OF WATER VAPOR ADSORPTION ON ZEOLITES

BADANIE EFEKTÓW TERMICZNYCH PODCZAS ADSORPCJI WODY NA ZEOLITACH

Abstract

Temporal variations of temperatures in an adsorbent bed have been studied in this paper. Separation of an ethanol-water vapor mixture on zeolites has been considered. Temperature of the bed was determined both experimentally and numerically on the basis of a mathematical model of the process. The conformity between experimental and numerical values was satisfactory. It was found that maximum temperature in the bed depends mainly on water content in the raw material.

Keywords: adsorption, thermal effects, ethanol dehydration, zeolites

Streszczenie

W artykule podano badania czasowych zmian temperatur w złożu adsorbentu. Pomiary dotyczyły rozdzielania parowej mieszaniny etanol-woda na zeolitach. Przebiegi temperatur złoża zostały określone zarówno eksperymentalnie, jak i obliczeniowo w oparciu o model matematyczny procesu. Zgodność wyników doświadczalnych i obliczeniowych była zadowalająca. Stwierdzono, że maksymalna temperatura w złożu zależy głównie od zawartości wody w odwadnianym surowcu.

Słowa kluczowe: adsorpcja, efekty cieplne, odwadnianie etanolu, zeolity

* MSc. Eng. Monika Gwadera, PhD. Eng. Associate Professor Krzysztof Kupiec, PhD. Eng. Associate Professor Jan Rakoczy, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

Zeolites belong to adsorbents which strongly adsorb water. Due to that fact, zeolite beds are often used for adsorptive drying of organic substances. Drying of fuel ethanol [1–14] is a typical example of such a process. This process is conducted in a gas phase. Adsorbent is regenerated by pressure reduction (Pressure Swing Adsorption process). The 3A-type zeolites, which selectively adsorb water from ethanol-water mixture, are used.

Adsorption causes heat production. Duration of each step of a cyclic adsorption-desorption process is the same. For this reason in initial cycles (conducted on fresh adsorbent) the bed is only slightly regenerated after a desorption step. Therefore, in initial cycles the bed adsorbs more water in adsorption steps than loses in regeneration steps. Only after a certain number of adsorption-desorption cycles the cyclic steady state is reached. Before that state is reached, especially in several or dozen or so initial cycles, temperature of the bed strongly increases in adsorption steps, and insufficiently decreases in desorption steps. This can cause severe local overheating of adsorbent pellets (bed). High temperatures are very disadvantageous because of the possibility of zeolites structure destruction what can lead to adsorptive properties breakage. What is more, under the influence of high temperature and catalytic properties of zeolites, carbon deposit which reduces sorption capacity of pellets forms.

In the case of ethanol dehydration the problem is of high practical importance and was described in literature [1]. In industrial practice, when adsorbent is fresh, the column is firstly fed with partially dehydrated raw material in order to reduce the effect of bed temperature increase. Only after some time water content in the raw material is being increased gradually until it reaches the target value.

In order to predict the maximum values of temperatures that can be reached during adsorption-desorption cycles on fresh adsorbent, it is convenient to conduct process simulation based on a mathematical model. Such a model should be firstly checked for its compatibility with reality. Such verification can be conducted e.g. for adsorption step under laboratory conditions.

The aim of this work is to present results of studies on temperatures of the bed for ethanol dehydration on zeolites under laboratory conditions and to compare these temperatures with values obtained on the basis of a mathematical model of the process.

2. Mathematical model of the process

The model of the process was based on the following assumptions:
- The mixture is composed of an inert component (ethanol) and adsorptively active component (water),
- The mixture behavior is governed by the ideal gas laws,
- The gas phase is flowing with the plug flow model,
- Physical properties of gas and solid phases do not depend on temperature,
- Gas-phase temperature and pellets temperature are the same in a given cross-section of the bed,
- Mass transfer resistance in the gas phase can be neglected,

- Mass transfer rate can be described with the LDF equation using concentration of a component in a pellet,
- Pressure drop of gas flowing through the adsorbent bed is low,
- Heat of adsorption is constant.

When the above assumptions are made, the general balance equation takes the form:

$$\frac{\partial u}{\partial z} + \frac{\rho_p \left(1-\varepsilon\right) RT_0}{M_w P} \cdot \frac{\partial \overline{q}_m}{\partial t} = 0 \qquad (1)$$

The balance equation for water has the form:

$$u \frac{\partial y_{mol}}{\partial z} + \varepsilon \frac{\partial y_{mol}}{\partial t} + \frac{\rho_p \left(1-\varepsilon\right) RT_0}{M_w P} \cdot \frac{\partial \overline{q}_m}{\partial t} = 0 \qquad (2)$$

while the heat balance equation:

$$u \frac{\partial T}{\partial z} + \left[\varepsilon + \frac{c_p \rho_p \left(1-\varepsilon\right) RT_0}{C_{mol} P} \right] \frac{\partial T}{\partial t} - \frac{\rho_p \left(1-\varepsilon\right) Q_{st} RT_0}{C_{mol} M_w P} \cdot \frac{\partial \overline{q}_m}{\partial t} + $$
$$ + \frac{4hRT_0}{d_c C_{mol} P} \left(T - T_w\right) = 0 \qquad (3)$$

The Dubinin-Raduschkevich relationship was used as an equation of adsorption equilibrium

$$q_m^* = q_{ms} \exp\left[-b \left(T \cdot \ln \frac{P_{sat}}{P y_{mol}} \right)^2 \right] \qquad (4)$$

Adsorption kinetics was described with the LDF equation

$$\frac{d\overline{q}_m}{dt} = \left(k_s a\right)\left(q_m^* - \overline{q}_m\right) \qquad (5)$$

Initial conditions refer to the system that does not contain the adsorptively active component (water) before the process starts:

$$0 \le z \le L, \qquad t = 0; \qquad \overline{q}_m = 0, \quad y_{mol} = 0, \quad T = T_0 \qquad (6)$$

Boundary conditions are determined by the values for the system feed:

$$z = 0, \quad t \ge 0; \qquad y_{mol} = y_{mol0}, \qquad T = T_0, \quad u = u_0 \qquad (7)$$

The model equations were solved using the finite difference method.

3. Experimental part

Experimental studies were conducted in the installation presented in Fig. 1. A column of a diameter 13.0 mm filled with pellets of zeolites to a height 330 mm was the main element of the installation. Before loading to the column, the pellets had been heated for 3 hours at 375°C and then had been cooled down. Three thermocouples were put into the column from its bottom. The thermocouples were located in the axis of the bed 50, 167 and 287 mm from the inlet of the raw material. Water vapor under atmospheric pressure (100°C) was fed into the jacket of the column. Before measurements, the bed was heated up to 100°C. Water solutions of ethanol of different concentrations were used as the raw material for the dehydration process. The raw material was fed from the top of the column with the use of a syringe pump (the 610-2 type). Before the raw material was fed into the column, it had been evaporated in an evaporator 3. When vapors of ethanol and water were flowing through the bed, only water was adsorbed. Ethanol vapors leaving the column were condensed and dehydrated ethanol was collected in the receiver. Temporal variations of temperatures at the three levels in the bed were determined during the process. Results of measurements were registered automatically.

Four series of measurements were conducted. Molar fractions of water in the raw material and raw material flow rates used in each measurement series are presented in Table 1.
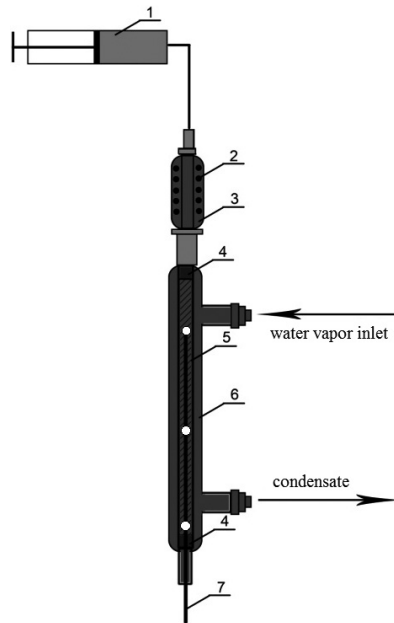

Fig. 1. Scheme of an experimental installation: 1 – dosing pump, 2 – heating coil, 3 – evaporator, 4 – stream stabilizer, 5 – adsorption column filled with zeolites, 6 – heating jacket, 7 – thermocouples

Rys. 1. Schemat instalacji badawczej: 1 – pompa dozująca, 2 – spirala grzejna, 3 – parownik, 4 – wyrównywacz strumienia, 5 – kolumna adsorpcyjna wypełniona ziarnami zeolitów, 6 – płaszcz grzejny, 7 − termopary

Values of process parameters and maximum temperatures for each series of measurements

Series	y_{mol0}	$\dot{m}_0$ [kg/h]	T_{max} [°C]
1	0.160	0.0815	150.8
2	0.288	0.0828	173.6
3	0.522	0.0868	180.3
4	0.522	0.0174	–

Temporal variations of bed temperatures at the three levels in the bed obtained for the four measurement series are presented in Fig. 2–5 in the form of symbols.
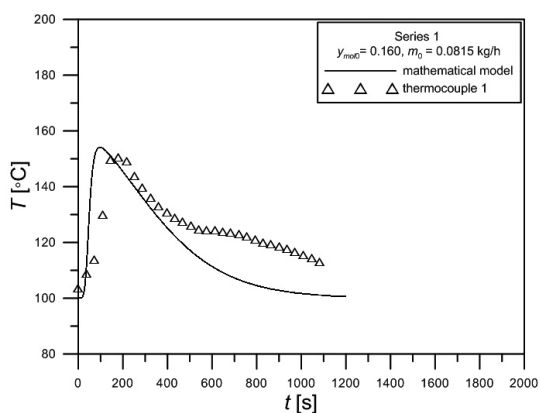

Fig. 2. Temporal variations of bed temperature – series 1

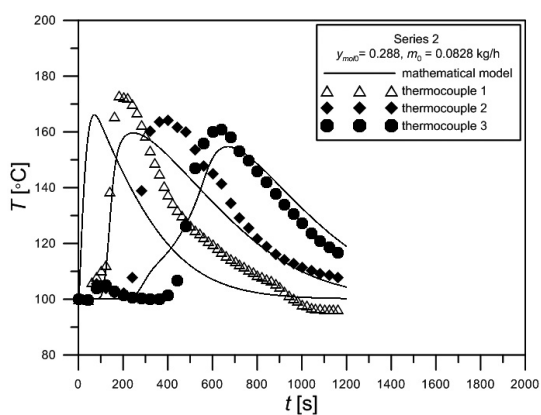Rys. 2. Czasowe zmiany temperatury złoża – seria 1

Fig. 3. Temporal variations of bed temperature – series 2

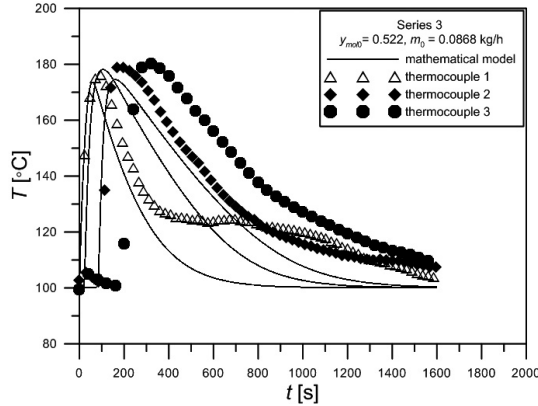Rys. 3. Czasowe zmiany temperatury złoża – seria 2

Fig. 4. Temporal variations of bed temperature – series 3
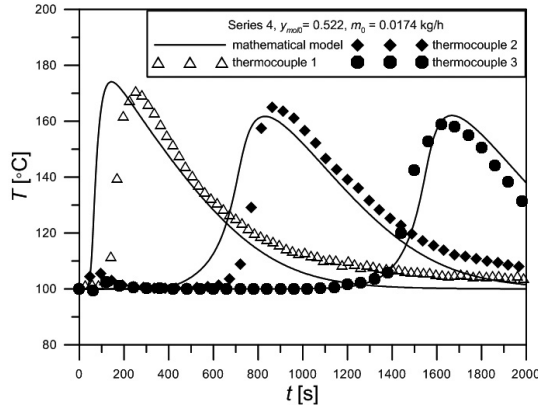
Rys. 4. Czasowe zmiany temperatury złoża – seria 3

Fig. 5. Temporal variations of bed temperature – series 4

Rys. 5. Czasowe zmiany temperatury złoża – seria 4

4. Analysis of temporal profiles of bed temperature

All temporal variations of temperature presented in Fig. 2–5 have the same shape. Initially the bed temperature increases, then reaches the maximum and finally decreases. Time required to reach the maximum depends on the bed height coordinate in the bed. The further from the bed inlet, the longer time needed to reach the maximum.

Maximum temperature increments depend on water content in the raw material: the more water is in the raw material, the higher temperatures are reached. For example maximum temperatures which was determined experimentally for the thermocouple 1 placed near the inlet and the raw material flow rate in the range of 0.0815 – 0.0868 kg/h are presented in the last column of Table 1.

Temperature runs presented in Fig. 2–5 were determined on the basis of a numerical solution of the equations of the mathematical model of adsorption in a column presented in Chapter 2. The following values of process parameters were used in calculations: $q_{ms} = 0.139$ kg/kg, $b = 2.33 \cdot 10^{-7}$ K^{-2}, $C_{mol} = 90$ J/(mol·K), $\rho_p = 1190$ kg/m^3, $c_p = 960$ J/(kg·K), $\varepsilon = 0.4$, $Q_{st} = 51900$ J/mol, $h = 25$ W/(m^{2}K), $d_c = 0.0130$ m, $k_s a = 0.008$ s^{-1}, $T_0 = 373$ K, $T_w = 373$K, $P = 10^5$ Pa, $P_{sat} = 1.013 \cdot 10^5$ Pa, $L = 0.330$ m.

On the basis of the figures it can be stated that the conformity between experimental and numerical runs is rather good, still there are discrepancies in some runs. They result from both measurement and model errors. The latter are primarily a consequence of simplifying assumptions listed at the beginning of Chapter 2. Moreover, some parameters of the model are encumbered with errors, what also influences the results of calculations. It should also be taken into account that differences between numerical and experimental values are not big and in terms of the qualitative criteria the model is fully adequate. Therefore, it can be concluded that the presented model is useful (after some adaptation) for prediction of bed temperatures during adsorption-desorption cycles. In this way maximum temperatures of the bed that may be expected in a cyclic process during start up of an installation can be estimated. Such tentative calculations were conducted and described in work [15].

5. Conclusions

1. Temperature increments in the range of 50–80K were obtained under the conditions of measurements. This gives maximum temperatures in the range of 150–180°C for the used inlet gas temperature $T_0 = 100$°C. The difference between values of maximum temperatures found experimentally and numerically is small.
2. Water content in the raw material had the major influence on bed temperature increments.
3. Comparing temporal variations of temperatures determined experimentally and numerically i.e., on the basis of the mathematical model of the process, for different process conditions and different height coordinates, one can conclude that the conformity is satisfactory. This confirms the correctness of the presented model.

S y m b o l s

c_p	–	specific heat capacity of adsorbent pellets [J/(kg·K)]
C_{mol}	–	molar heat capacity of a gas phase [J/(mol·K)]
$k_s a$	–	coefficient of mass transfer in a pellet [s^{-1}]
h	–	coefficient of heat transfer between a bed and wall [W/(m^2·K)]
L	–	bed height [m]
M_w, M_{et}	–	molar mass of water and ethanol respectively [kg/mol]
p	–	water vapor partial pressure [Pa]
P_{sat}	–	saturated water vapor pressure [Pa]
P	–	total pressure [Pa]
$\overline{q}$	–	water content in pellets [kg/kg]
q_m^*	–	water content in pellets in equilibrium with concentration in a gas phase [kg/kg]

Q_{st}	–	isosteric heat of adsorption [J/mol]
t	–	time [s]
T	–	temperature [K]
u	–	superficial velocity of gas [m/s]
y_{mol}	–	molar fraction of a component in a gas phase [–]
z	–	bed height coordinate [m]
ε	–	bed porosity [–]
ρ_p	–	superficial density of pellets [kg/m^3]

Indexes:

0	–	inlet
w	–	wall

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