PhD dissertation

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Experimental studies and modeling of the cyclic pressure swing adsorption process for gas separation on a multilayer bed

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Summary

The paper presents the results of literature, experimental and model studies of the pressure swing adsorption column process (PSA) for a gas mixture on a single- and double-layer bed. The gas mixture consisted of carbon dioxide (CO_2), nitrogen (N_2) and water vapor (H_2O), and the adsorbents were zeolite molecular sieves of two types: 13X and 3A with a granulation of 1/16". The work consists of three main parts: literature review, experimental research and process modeling.

The literature part discusses the methods of separation of gas mixtures, including those related to carbon dioxide capture, where the main focus was on adsorption processes and adsorbents, which should be characterized by high selectivity and adsorption capacity in relation to the removed component. The literature section describes the process equilibrium and models of adsorption isotherms, energy effects and isosteric heat of adsorption, process speed and models of adsorption kinetics, fixed bed adsorption dynamics and methods of spent adsorbent regeneration. In practice, column installations operating in adsorption-desorption cycles at variable temperatures and/or pressures are used to separate gases by adsorption. The paper discusses modifications of cyclic adsorption processes, focusing mainly on the PSA pressure swing adsorption process, which was used in own experimental studies. The current state of knowledge on mathematical modeling, which includes mass and heat balances, is presented, and their solution requires taking into account initial and boundary conditions based on literature data and experimental research. Based on the literature review, it was found

that although mathematical modeling can be a useful tool in plant design, it requires a more complete understanding of the process for a specific adsorption system. The aim of the work was to extend knowledge in the field of the cyclic PSA pressure swing adsorption process, applicable to the separation of difficult to adsorb gases, on the example of carbon dioxide removal from streams containing nitrogen and water vapor.

In the experimental part, gaseous adsorbates selected for testing were characterized: carbon dioxide, nitrogen and water vapor, as well as adsorbents: zeolite 13X and 3A. The studies of adsorption kinetics and equilibrium were carried out in a wide range of temperatures (293-393 K) and pressures (2000 kPa) using the static gravimetric method on the IGA-002 Intelligent Gravimetric Analyzer (Hiden Isochema, Great Britain). The highest value of the carbon dioxide adsorption capacity is 5,44 mol/kg for 2000 kPa, while for nitrogen it is 1,77 mol/kg under the same process conditions. The adsorption of carbon dioxide from the mixture on zeolite 13X is more than three times higher than the adsorption of nitrogen. The adsorption capacity for water vapor is 15,93 mol/kg and was obtained at a temperature of 293 K and a pressure of 2,104 kPa. For the carbon dioxide – zeolite 3A system, the adsorption capacity is 4,33 mol/kg (293 K; 2000 kPa), and for water vapor is 10,07 mol/kg (293 K; 1,87 kPa). The obtained equilibrium data were developed using multi-temperature isotherm models: Langmuir, Langmuir-Freundlich and Toth. The best fit was obtained using the Langmuir-Freundlich isotherm model. The study of the process speed showed that carbon dioxide adsorbs the fastest on the zeolite 13X, and water vapor the slowest.

Process kinetic studies were conducted on zeolite 3A for carbon dioxide, which showed that carbon dioxide adsorbed the fastest on the 13X zeolite, and water vapor the slowest. Process speed studies were carried out on zeolite 3A for carbon dioxide, which showed that its adsorption time on this zeolite is 150 times longer than on zeolite 13X. Pseudo-first and pseudo-second kinetics models were selected to describe the kinetic curves, only the latter matched the experimental data well. Model parameters were selected using non-linear estimation in Statistica 13.1 (Statsoft). The thesis was put forward that, the problem of the effect of moisture on the adsorption of carbon dioxide on zeolite 13X can in practice be solved by using an additional desiccant layer of zeolite 3A in which the moisture contained in the mixture is removed.

The tests of carbon dioxide separation from a model gas mixture with nitrogen and steam were carried out in a single-column installation with an internal diameter of 0,026 m with one or two beds piled up to a height of 0,50 m equipped with a heating jacket. This installation was used to carry out tests in three configurations: (i) preliminary tests of the TPSA process

on zeolite 13X for two components, i.e. carbon dioxide and nitrogen with the use of heating supporting bed regeneration and basic tests of the PSA process: (ii) with one adsorbent bed (zeolite 13X) for a binary mixture (CO_2, N_2) and a ternary mixture (CO_2, N_2, H_2O), (iii) with a two-layer bed of adsorbents (zeolite 13X and zeolite 3A) for a ternary mixture (CO_2, N_2, H_2O). During the measurements, pressures, temperatures and flows were regulated and recorded and the composition of individual gas streams at the inlet and outlet of the column was analyzed. As a result of the column tests, concentration and temperature profiles were obtained for each of the adsorption and desorption stages, which were used to determine the breakthrough and bed saturation times and other parameters important for the analysis of the column operation. The obtained test results were used to validation model the cyclic pressure swing adsorption process.

In the last stage of the work, a mathematical model of the PSA pressure swing adsorption process for the separation of carbon dioxide from the gas mixture with nitrogen and water vapor in a column with a single- and double-layer adsorbent bed was developed. The mathematical model contained the following equations: components mass balances, linear driving force model, energy balances for solid and gaseous phases, adsorption equilibrium model. The system of second-order partial differential equations was solved using the numerical line method using Matlab R2021b (MathSoft, USA). Then, the results of the calculations were verified experimentally, confirming the usefulness of the developed model to describe the PSA process. Validation of computer simulation results of PSA process dynamics carried out using own experimental results confirmed good agreement for all tested configurations of gas streams and the number of layers of adsorbents.

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