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Anhydrous ethanol recovery from wet air in TSA systems – Equilibrium and column studies

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HIGHLIGHTS

- Adsorption equilibrium water and ethanol on ACS4 and ZMS3A are presented.
- Multi-temperature isotherm models are developed for tested adsorption systems.
- Energetic effects of the adsorption are determined.
- Two combined TSA systems for recovery anhydrous ethanol from wet air are compared.

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ABSTRACT

An experimental and theoretical study of two combined temperature swing adsorption (TSA) systems for the recovery of anhydrous ethanol from wet air using activated carbon Sorbonorit 4 (ACS4) and zeolite molecular sieve 3A (ZMS3A) are developed. Adsorption isotherms of ethanol and water vapors on ACS4 and ZMS3A in the temperature range of 20–140 °C and water from liquid ethanol on ZMS3A at temperatures of 20–60 °C were measured. The data were analyzed using multi-temperature Toth, Sips, hybrid Langmuir-Sips, inhomogeneous DA and the excess surface work models. The results demonstrate selective water adsorption on ZMS3A with higher adsorption capacity in the liquid (28.02 mol/kg) than in the gas phase (10.67 mol/kg), and higher adsorption of ethanol (7.21 mol/kg) than water vapor on ACS4 up to relative pressure 0.6. The influence of the inlet concentration in the gas (2.8–8.4 g/m^3 for ethanol) and liquid phase (45–141 kg/m^3 for water–ethanol mixture) on the adsorption dynamic was studied in two fixed-bed columns with ACS4 and ZMS3A. The characteristic parameters of breakthrough curves and maximum temperature rise in the column were determined. The Thomas model was successfully employed to predict the breakthrough curves for both gas and liquid phase. The energy requirement for ethanol electrothermal desorption from ACS4 bed (151–235 kJ/mol) was lower than for hot purge gas regeneration of wet ZMS3A bed (423 kJ/mol). These values were several times larger than the isosteric heat of adsorption (13–71 kJ/mol) which represents minimum energy requirement for desorption.

1. Introduction

Ethanol is an important organic compound widely used in various branches of industry. The typical industrial alcohol applications are: chemicals, food and petroleum products, fungicides, laboratory reagents, plastics, antiseptic and preserving solutions, refrigeration, solvents and thinners [1,2]. The possibility of ethanol application as reagent and solvent depends on its purity. Due to the low normal boiling point and the high volatility, the use of ethanol (as any of the volatile organic compounds – VOCs) leads to large losses and air pollution [2,3]. The recovery and reuse of ethanol can help to reduce fresh solvent requirements [4].

The adsorption process is well suited for purifying waste gas streams which contain low concentrations of pollutants. Activated carbon is the preferred adsorbent for most VOCs recovery because of its low cost and high adsorption capacity [5]. However, the adsorption of ethanol from air on activated carbon is problematic in the presence of moisture. It reduces the adsorbent capacity and the quality of the recovered ethanol [4].

Recovery solvent vapors from waste gas streams may be performed with cyclic temperature swing adsorption (TSA) processes [6–9]. The conventional process consists of two main stages: adsorption on activated carbon and regeneration with hot gas, where the former stage is carried out at ambient temperature

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and the latter – in a high temperature range. The ethanol–water mixture is recovered as a condensate after a thermal desorption step. If the solvent and water are miscible (such as ethanol), an additional liquid separation process is used to recover the anhydrous solvent, usually in the form of simple distillation. Distillation is an energy consuming process and the separation of a mixture of ethanol and water is limited by the concentration of the azeotropic mixture (about 95 wt%). The ethyl alcohol dewatering in the concentration range of 95–99.5 wt% can be conducted in the process of azeotropic distillation, pervaporation and adsorption on zeolite [10–15].

The adsorption process efficiency in the TSA system depends on the proper selection of adsorbents and the fixed-bed operating conditions. The preliminary selection of adsorbents was made on the basis of their physical properties and a range of applications. The chemical characteristics of the separated compounds (ethanol, water) were also taken into account. The primary requirements for adsorbents include: sufficient adsorption capacity, appropriate selectivity as well as physical, chemical and thermal stability [4].

This paper presents two configurations of combined TSA process to recovering anhydrous ethanol from wet air. Both variants consist of four steps. In the first system (Fig. 1a), adsorption takes place in both gas and liquid phases, and consists of the following steps: (i) adsorption of ethanol and water vapors from waste gases on ACS4 (ii) desorption of the vapor mixtures, (iii) condensation of vapor mixtures, (iv) dewatering of liquid mixtures on ZMS3A in second column. In the other system (Fig. 1b.), adsorption takes place only in gas phase, and consists of: (i) dewatering waste gas stream on ZMS3A, (ii) adsorption of ethanol vapor on ACS4, (iii) desorption of pure ethanol vapor from ACS4 and (iv) condensation of desorbate.

In variant I (Fig. 1a), ethanol and water vapors are adsorbed in the first column with ACS4 fixed-bed. A mixture of water–ethanol obtained in the regeneration stage is subsequently dewatered by adsorption from the liquid phase in the adsorber with the ZMS3A fixed- bed. Therefore, the distillation unit is replaced by a supplementary TSA system. In variant II (Fig. 1b), the polluted air is dewatered in the first column filled with ZMS3A. Then the ethanol vapors are removed from air stream in the column with ACS4. The individual compounds are adsorbed in the separated column. Thus, during the regeneration of the ACS4 bed the anhydrous ethanol is recovered, which does not require further treatment.

The suitability evaluation of the two suggested variants of the anhydrous ethanol recovery process will be conducted based on the single-component equilibrium measurement and dynamic study of adsorption. On this basis, the adsorption capacity of both adsorbents will be compared in a wide range of temperatures and concentrations of the two compounds. Four multi-temperature isotherm equations will be used to fit experimental data. The energy effects of the adsorption process will be estimated using the excess surface work model (ESW) [16,17]. There are significant indicators of a strength interaction between the adsorbate molecules and the adsorbent, which will provide information about the adsorption mechanism. Characteristic parameters of the adsorbent fixed-bed will be determined based on breakthrough tests. All data are useful for the design of adsorption systems.

The aims of the work presented herein are: (i) determination of adsorptive capacity of selected adsorbents for water and ethanol in gas and liquid system, (ii) determination of best-fit multi-temperature isotherm models, (iii) determination of the effects of the adsorption energy, (iv) the modeling of breakthrough curves obtained in two different TSA systems, (v) comparison of the two combined TSA systems for the recovery of anhydrous ethanol from a wet gas stream.

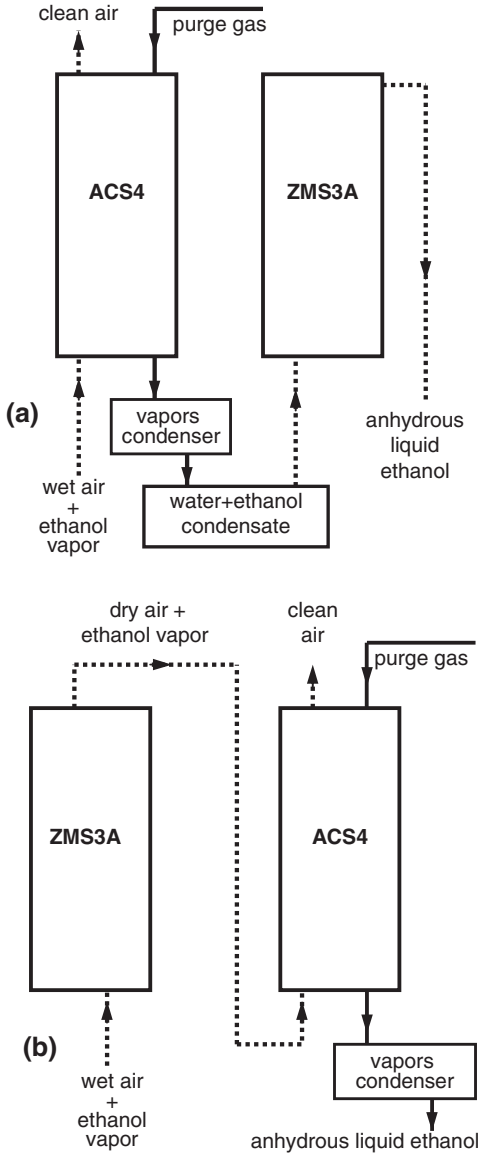

Fig. 1. Two variants of the combined TSA processes characterized by: (a) competitive adsorption of ethanol and water vapors on ACS4 bed and final treatment of liquid ethanol in dewatering step on ZMS3A bed, (b) selective adsorption of water vapor on ZMS3A bed and ethanol recovery from ACS4 bed in the desorption step (dotted line: adsorption step; solid line: desorption step).

2. Experimental

2.1. Materials

Ethanol analytical grade purity 99.7%, purchased from Chempur, (Poland) was used as adsorbate. Distilled water was used to prepare a solution of ethanol and for saturating the air with water vapor. ZMS3A in the form of beads with the approximate diameter of 1/16-in. (Sigma–Aldrich, USA) were used as adsorbent [13,18,19]. ACS4 was purchased from Norit Americas Inc., Netherlands. It is a steam activated extruded carbon with cylindrical particles with the diameter of 3.8 mm and length of 5–13 mm. Owing to its favorable adsorption properties (total surface area B.E.T. 1400 m^2/g), it is applied in solvent recovery applications [20].