Modelling of Adsorptive-distillation of Ethanol-water Using Natural and Synthetic Zeolites as Adsorbent

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ABSTRACT: *The purpose of this research is to study the modeling of adsorptive-distillation (AD) on ethanol-water mixture purification using natural and synthetic zeolites as adsorbent. The synthetic zeolite type used was zeolite 3A. AD is an effective way to purify ethanol-water mixture so that it can produce pure ethanol as fuel. Natural and synthetic zeolites as adsorbent are quite promising for industrial application. The experiment was conducted in a batch operation. Four AD modellings are developed based on four different simplifications, i.e., quasi-steady-state with no axial dispersion (Model 1), unsteady-state with no axial dispersion (Model 2), quasi-steady-state with axial dispersion (Model 3) and unsteady-state with axial dispersion (Model 4). The equilibrium equation correlating water content in vapour and water content in adsorbent particle was approximated by Henry's law model.*

Keywords: Adsorptive-distillation, axial dispersion, ethanol-water, modelling, zeolite

1.   INTRODUCTION

Azeotropic distillation is mostly conducted by combination of distillation and adsorption of the vapour-phase. This process is often called adsorptive-distillation (AD).[1] The principle of AD method is to break the azeotropic point by letting the undesired component trapped on the adsorbent based on adsorption phenomena,

so that the desired product rises in composition passing the azeotropic point. This process can be applied for ethanol-water mixture.[2] Ethanol has been part of chemicals and beverages for a long time, but its application has expanded during the 20th century. One of the chemical products expanded is in the use of ethanol as fuel.[3] Ethanol as replacement or substitution for conventional fuel will help to overcome energy crisis and curb CO_2 emission.[4,5] Since ethanol fuel could also be produced from lignocellulose, it can reduce lignocellulosic biomass waste, as well as avoid CO_2 emission accumulation.[6–8] However, the challenging process in ethanol fuel production is the separation of ethanol-water mixture to produce absolute ethanol.[9] In conventional processes, ethanol concentration produced by fermentation and followed by multi-stages distillation is about 96.5% v/v. Therefore, this ethanol must be concentrated to anhydrous concentration.[10,11]

In AD method, water vapour resulted from distillation process is adsorbed simultaneously so that the azeotropic point can be passed.[12] This method is more economical and efficient than others.[13–15] The latter workers used inorganic adsorbents such as molecular sieves, lithium chloride, silica gel and activated alumina.[4,9,14,16,17] In addition, synthetic zeolites 3Å is better than natural ones for removing and purifying ethanol from an ethanol-water mixture in gas phase.[16] The focus of this research is to study the quantitative modelling of adsorptive-distillation of ethanol-water solution using natural and synthetic zeolites as adsorbent.

The adsorption is conducted in a column packed with adsorbent. In the adsorption zone, transfer mechanism of the adsorbed component (i.e., water) from the bulk fluid (i.e., ethanol-water vapour mixture) into the adsorbent's surface must be known. In principle, the mechanism will be the following series of steps: (1) mass transfer from the bulk fluid to the external surface; (2) diffusion from the external surface through the pore; (3) mass transfer from the bulk fluid in the pore to the wall of pore or internal surface; and (4) adsorption into the internal surface. However, in most cases, steps 3 and 4 occur quite fast compared with steps 1 and 2 hence the rate of adsorption process is usually controlled by 1 or 2, or both. Some assumptions and basic concepts above will be applied in the development of the following AD model.[18]

The component adsorbed was assumed to be only water. Therefore, the ethanol component does not change. Hence, the mass balance is expressed by water component that flows in AD. Completely, the water mass balance can be expressed as follow (rate of input – rate of output = rate of accumulation):

$$\left[-Dax.S.\frac{\partial C_A}{\partial x}\Big|_x + F.C_A\Big|_x\right] -$$
$$\left[-Dax.S.\frac{\partial C_A}{\partial x}\Big|_{x+\Delta X} + F.C_A\Big|_{x+\Delta x} + k_c.a\,(C_A - C_A*)\,S.\Delta x\right] \qquad (1)$$
$$= S.\Delta x.\varepsilon\frac{\partial C_A}{\partial t}$$

where D_{ax} is axial dispersion coefficient (dm^2 min^{-1}), F is vapour volumetric rate (l min^{-1}), S is cross-section area of the column (dm^2), x is axial position in bed (m), ε is porosity of bed of adsorbent, $k_c.a$ is volumetric mass transfer coefficient (1 min^{-1}), C_A is water concentration (mol l^{-1}), and $C_A{}^*$ is concentration of water in the vapour at equilibrium to that on the surface of adsorbent (mol l^{-1}). C_A* is assumed to follow Henry's law as in Equation 2:[2]

$$C_A* = HX_A \qquad (2)$$

where X_A is water content in the adsorbent (mol water g^{-1} adsorbent), while H is equilibrium constant of Henry (g ads l^{-1}). Since the water content in the vapour is relatively low, the value of F is assumed to be constant. The mass balance of water on the adsorbent at the volume element of bed between x and $x+dx$ can be expressed as in Equation 3:

$$\frac{\partial X_A}{\partial t} = \frac{k_c.a}{\rho_b}(C_A - C^*_A) \qquad (3)$$

where ρ_b is bulk density of adsorbent (g ads l^{-1}).

The parameters of mass transfer coefficient ($k_c a$), Henry's constant (H), and axial dispersion coefficient (D_{ax}) can be calculated using curve-fitting method.

With commutative law, Equation 1 is rewritten as in Equation 4.

$$\frac{\frac{\partial C_A}{\partial x}\Big|_{x+\Delta x} - \frac{\partial C_A}{\partial x}\Big|x}{\Delta x} - \frac{F}{S.Dax}\left[\frac{C_A\Big|_{x+\Delta x} - C_A\Big|_x}{\Delta x}\right] \qquad (4)$$
$$-\frac{kc.a}{Dax}[C_A - C_A^*] = \frac{\varepsilon}{Dax}\frac{\partial C_A}{\partial t}$$

If Δx approaches to zero, the above equation can be simplified as Equation 5:

$$\frac{\partial^2 C_A}{\partial x^2} - \frac{F}{S.Dax}\frac{\partial C_A}{\partial x} - \frac{kc.a}{Dax}[C_A - C_A^*] = \frac{\varepsilon}{Dax}\frac{\partial C_A}{\partial t} \qquad (5)$$

2.   EXPERIMENTAL

The accuracies of the models proposed were verified by experimental data. The data were obtained from AD of ethanol-water with operating condition as follows. Ethanol-water mixture as raw material (93.8% v/v) was put in a flask and then heated until gradually evaporated. The vapour formed was fed to a vertical column adsorbent. The value of C_{A0} (concentration of water entering the column) was calculated from the correlation of liquid-vapour equilibrium (LVE) curve of ethanol-water system under the azeothrope point. Thus, C_{A0} was about 5.72 mol l^{-1}. The shape of natural and synthetic zeolites was assumed to be spherical with particle diameter of 3–5 mm. The designed AD apparatus was similar to the one used in the experiments conducted by Boonfung and Rattanaphanee.[10] The zeolites as adsorbent was packed in column with an inside diameter of 2.54 cm and a length of 10 cm. The adsorbent column was insulated with asbestos fibre tape in order to avoid energy loss in the environment. The distillation process was conducted in a 500 ml flask filled with 300 ml ethanol-water mixture and then heated by 515 W electric heating mantle (SCILOGEX MS-H280-Pro). Power input of heating mantle was controlled by a power regulator to achieve a constant temperature of 78°C. This temperature was recorded using thermocouple attached in one of the nozzle on the flask. In the AD process, the ethanol-water vapour flows into adsorber column and then the vapour leaving the column was condensed by 28°C water as the cooling medium. The condensates were collected in a bottle every 5 min. Thus, the process was conducted in batch operation, i.e., no ethanol-water solution added into the flask.

In the modelling of the AD system (Figure 1), to avoid complexity, the following simplifications were applied: liquid and vapour in the flask columns are in equilibrium state; holdup liquid in bed of adsorbent is neglected; adsorbent (natural and synthetic zeolites) adsorbs water only (single-component adsorption); and flow rate and density (average molecular weight) of ethanol-water solution are constant.
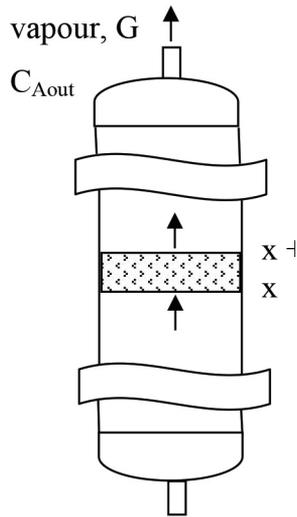
Figure 1: The element volume of mass transfer of water in adsorber column.

The data of ethanol concentration obtained is expressed in Table 1.[16]

Table 1:   Ethanol concentration in the vapour leaving the column (conditions: pressure 1 atm, heater temperature 160°C for Natural Zeolite and 19.64 g Zeolite 3Å, heater temperature 170°C for 15.39 g Zeolite 3Å)

(Concentration, mol l^{-1}) (Volume, ml) (Time, min)		
Natural Zeolite	Zeolite 3A (19.64 g)	Zeolite 3A (15.39 g)
(94.280) (0.0) (47)	(94.280) (0.0) (43)	(94.290) (0.00) (45)
(96.964) (1.4) (52)	(96.882) (1.8) (48)	(97.472) (11.8) (50)
(96.184) (1.8) (57)	(96.765) (1.7) (53)	(97.359) (12.0) (55)
(96.042) (2.0) (62)	(96.574) (1.7) (58)	(97.389) (12.0) (60)
(95.970) (1.8) (67)	(96.671) (1.4) (63)	(95.969) (11.8) (65)
(95.766) (1.6) (72)	(96.590) (1.5) (68)	(96.894) (12.2) (70)
(95.553) (1.6) (77)	(96.502) (1.5) (73)	(96.173) (12.4) (75)
(95.461) (2.0) (82)	(96.411) (1.4) (78)	(96.695) (12.0) (80)
(95.368) (1.6) (87)	(96.283) (1.4) (83)	(96.450) (12.0) (85)
(95.316) (2.2) (92)	(96.203) (1.2) (88)	(96.623) (11.0) (90)
(95.144) (2.0) (97)	(96.152) (1.2) (93)	(96.339) (11.9) (95)

In this research, the mass balance of AD was developed in several models, such as quasi-steady-state with no axial dispersion (Model 1), unsteady-state with no axial dispersion (Model 2), quasi-steady-state with axial dispersion (Model 3), and unsteady-state with axial dispersion (Model 4). Model 4 is very complete as in Equation 5.

At quasi-steady-state condition, the ethanol accumulation in column is negligible. The mass balance of water during the process with assumption of no axial dispersion is generated by setting the value of $D_{ax} = 0$. Therefore, Equation 5 can be simplified as Equation 6 for Model 1:

$$\frac{F}{S.\varepsilon}\left[\frac{\partial C_A}{\partial x}\right] + \frac{k_c.a}{\varepsilon}(C_A - C_A^*) = 0 \qquad (6)$$

As the same rule, assuming no axial dispersion at unsteady-state condition (Model 2), the mass balance is expressed by Equation 7:

$$\frac{F}{S.\varepsilon}\left[\frac{\partial C_A}{\partial x}\right] + \frac{k_c.a}{\varepsilon}(CA - C_A^*) = -\frac{\partial C_A}{\partial t} \qquad (7)$$

Meanwhile, the mass balance of water during the process with assumption of with axial dispersion at squasi-steady-state condition (Model 3) is generated as in Equation 8:

$$\frac{\partial^2 C_A}{\partial x^2} - \frac{F}{S.Dax}\frac{\partial C_A}{\partial x} - \frac{kc.a}{Dax}[C_A - C_A*] = 0 \qquad (8)$$

3.   RESULTS AND DISCUSSION

From the experimental results, it can be confirmed that the designed AD equipment can be used to purify ethanol. In this system, adsorbed water molecule was in vapour phase. The AD method in vapour phase was also conducted by Boonfung and Rattanaphanee.[10] The AD process was operated in semi batch-wise. Banat et al. investigated the ethanol purification in a fixed bed. This process resembles a batch distillation under unsteady-state condition. The average condensate flow rate achieved by manipulating power supply was ca. 1.5 ml min^{–1}.[19] On the other hand, Chen and Sheng carried out AD method to purify ethanol solution in liquid phase which was combined with water desorption using a high-temperature gas (i.e., nitrogen) in order to regenerate zeolite adsorbent.[11] Mujiburohman et al. studied purification of isopropanol-water using AD method in batch system.[14] The system was constructed with three columns, i.e., first distillation column to decrease water content until azeotropic point, bed of adsorbent as second column to remove water

in solution, and second distillation column as third column to purify isopropanol until anhydrous concentration.[17]

In this research, the initial ethanol concentration in the flask was 93.8% v/v (in liquid-phase). The concentration of ethanol condensate is equal to the vapour-phase ethanol concentration that was found from vapour-liquid equilibrium table at pressure of 1 atm and its value was about 94.28% v/v (the water content in first condensate was about 5.72% w/w). The value was far lower than its azeotropic point. Highest ethanol concentration achieved was 96.96% v/v (above the azeotropic concentration). Subsequently, if the initial ethanol concentration is close to the azeotrope point (near 96.5% v/v), the ethanol concentration produced from these experiments could achieve almost anhydrous ethanol.[16] Therefore, natural and synthetic zeolites are considered as promising adsorbents of water vapour in AD system.

Theoretically, zeolite has Si and Al components.[20] Natural and 3Å synthetic zeolites which have a pore size of about 0.4 nm can easily adsorb the water molecules that have a molecular diameter of 0.28 nm. While ethanol, with a molecular diameter of 0.44 nm, cannot be adsorbed by zeolites. Al-Asheh et al. studied the use of various molecular sieve adsorbents to dehydrate the ethanol-water mixture and to compare each other.[13] They found that a molecular sieve 3Å is the best solid adsorbent than that of 4Å and 5Å to adsorb the water content.[11] Their finding is also in a good agreement with study by Sowerby and Crittenden.[21] As a result, the molecular sieve 3Å adsorbent is widely used in ethanol purification.[15]

According to Chopade et al., zeolite is a mineral consisting of $SiO_2.AlO_2$ groups and alkali-ions.[22] In its complex crystal structure, zeolite is capable of adsorbing water vapour. Water content up to 25% (g water/g zeolite) can be adsorbed. From their experimental research, the water uptakes for 15 min, 30 min, 45 min and 60 min were 9.5%, 6%, 10.5% and 12.5%, respectively. In this research, at 50 min, the water uptakes of natural and synthetic zeolites were about 1.7% and 3.3%, respectively. The value of synthetic zeolite was greater than from cassava-based adsorbent (3.0%), but lower than from molecular sieve 3Å by Alameda et al. (13%) as well as from cornmeal adsorbent (11.5%).[23,24]

The good result achieved from this AD system was also due to adsorbent preparation prior to using it. The two preparation steps were activated using NaOH solution and heating in oven. Chemical treatment on the zeolite adsorbent activation can be done by acid and base treatment using HNO_3, HCl or H_2SO_4, and NaOH.[25] Basically, acid treatment could increase the Si/Al ratio. According to Abdullah, zeolite is activated using HCl or NaOH to increase the adsorption capacity.[26] Calcination

is the process of heating an object until the high temperature but still below the melting point to eliminate compounds that can evaporate. Zeolite activation process through calcination will release water and increase crystallinity. Therefore, calcination of natural zeolite can improve the specific properties of zeolite.

A state of the art of this research, a so-called modelling of adsorptive-distillation of ethanol-water mixture, was solved to describe the AD process especially to handle design application and scale-up. From the experimental result, AD was proved to be able to break up the azeotropic, although the ethanol concentration was far from anhydrous point, because the initial ethanol concentration was not near the azotropic point. Many literature studies have presented examples of modelling of distillation or adsorption phenomena.[2,27,28] In this research, the several mathematical models with different simplifications were applied.

Equation 6 is a partial differential equation which can be solved numerically using finite difference approximation principles (explicit method) in which this differential equation is converted into algebraic equation as in Equations 9 and 10 for i = 0 to N–1 and i = N (Model 1).

$$-(u' - v')C_{Ai,j} + u'C_{Ai+1,j} - v'C_A^* = 0 \tag{9}$$

$$u'C_{AN-1,j} - (u' - v')C_{AN,j} - v'C_A^* = 0 \tag{10}$$

Meanwhile, the results of the algebraic equations for Model 2 for i = 0 to N–1 as well as i = N are as in Equations 11 and 12.

$$-\left(\frac{1}{\Delta t} + u' - v'\right)C_{Ai,j} + u'C_{Ai+1j} - v'C_A^* = -\frac{1}{\Delta t}C_{Ai,j+1} \tag{11}$$

$$-\left(\frac{1}{\Delta t} + u' - v'\right)C_{AN,j} + u'C_{AN-1j} - v'C_A^* = -\frac{1}{\Delta t}C_{AN,j+1} \tag{12}$$

where:

$$u' = \frac{F}{S.\varepsilon(\Delta x)}, v' = \frac{kc.a}{\varepsilon}$$

Model 3 was solved using Equation 13 for i = 1 to N–1.

$$C_{Ai-1,j} + (-2 + u(\Delta x) - v)C_{Ai,j} + (1 - u(\Delta x))C_{Ai+1,j} + vC_A^* = 0 \tag{13}$$

For i = 0, with the assumption that $C_{Ai-1,j} = C_{A0}$ (no adsorption beyond the adsorbent bed), Equation 13 can be expressed as:

$$(-1 + u(\Delta x) - v)C_{A0,j} + (1 - u(\Delta x))C_{A1,j} + vC_A^* = 0 \tag{14}$$

With the assumption that $C_{AN+1,j} = C_{AN,j}$ (no adsorption beyond the adsorbent bed), the ethanol concentration at i = N can be expressed as Equation 15:

$$C_{AN-1,j} + (-1 - v)C_{AN,j} + vC_A^* = 0 \tag{15}$$

On the other hand, Model 4 was solved using Equation 16 for i = 1 to N–1.

$$C_{Ai-1,j} + (-2 + u(\Delta x) - v + Mo)C_{Ai,j} + \\ (1 - u(\Delta x))C_{Ai+1,j} + vC_A^* = MoC_{Ai,j+1} \tag{16}$$

For i = 0, Equation 16 can be expressed as Equation17:

$$(1 - + u(\Delta x) - v + Mo)C_{A0,j} + (1 - u(\Delta x))C_{A1,j} + vC_A^* = MoC_{A0,j+1} \tag{17}$$

For i = N, Equation 16 can be expressed as Equation 18:

$$C_{AN-1,j} + (-1 - v + Mo)C_{AN,j} + vC_A^* = MoC_{AN,j+1} \tag{18}$$

where:

$$Mo = \frac{\varepsilon(\Delta x)^2}{Dax(\Delta t)}, u = \frac{F}{S.Dax}, v = \frac{kc.a(\Delta x)^2}{Dax}$$

The results of calculation are shown in Figures 1 and 2. The figures showed that the models with axial dispersion (Models 3 and 4) can describe adsorption mechanism better than the ones without dispersion (Models 1 and 2) for natural and synthetic zeolites as adsorbent.
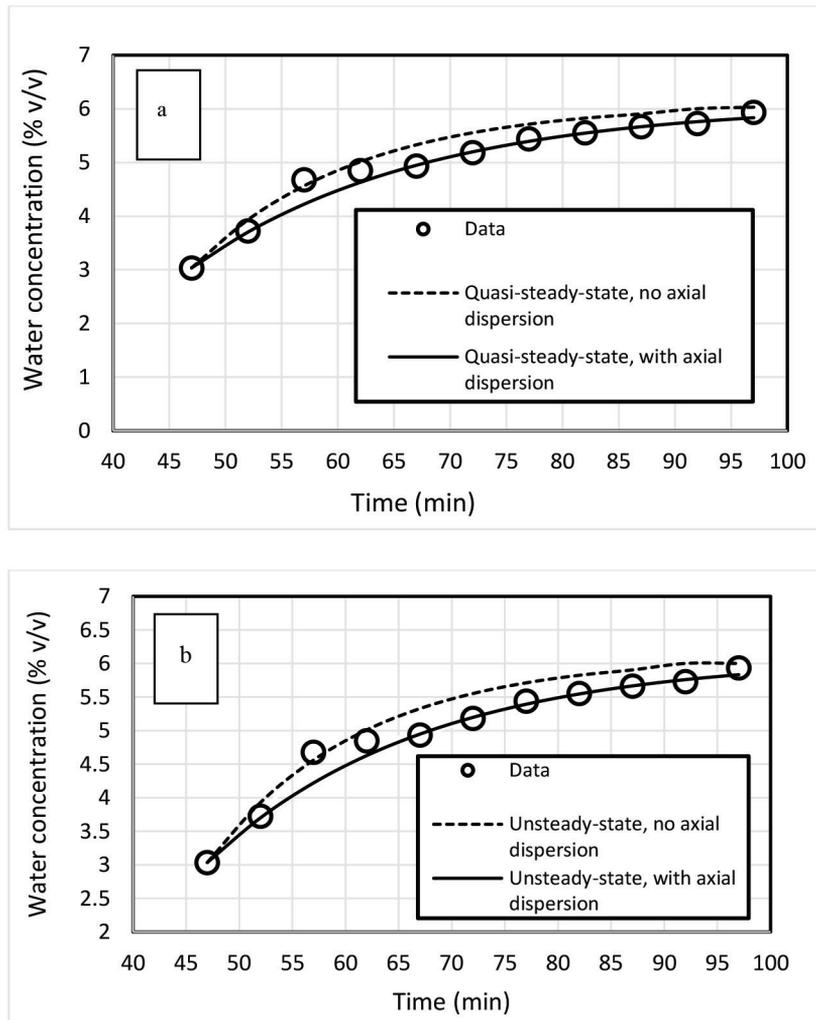
Figure 2:   Comparison of water concentration in volume fraction based on the experimental measurements and calculation of various AD models using natural zeolite as adsorbent with assumption in quasi-steady-state: (a) as well as unsteady-state; (b) at conditions: heating temperature of 160°C, pressure of 1 atm and condensate flows of 0.37 ml min^{-1}.
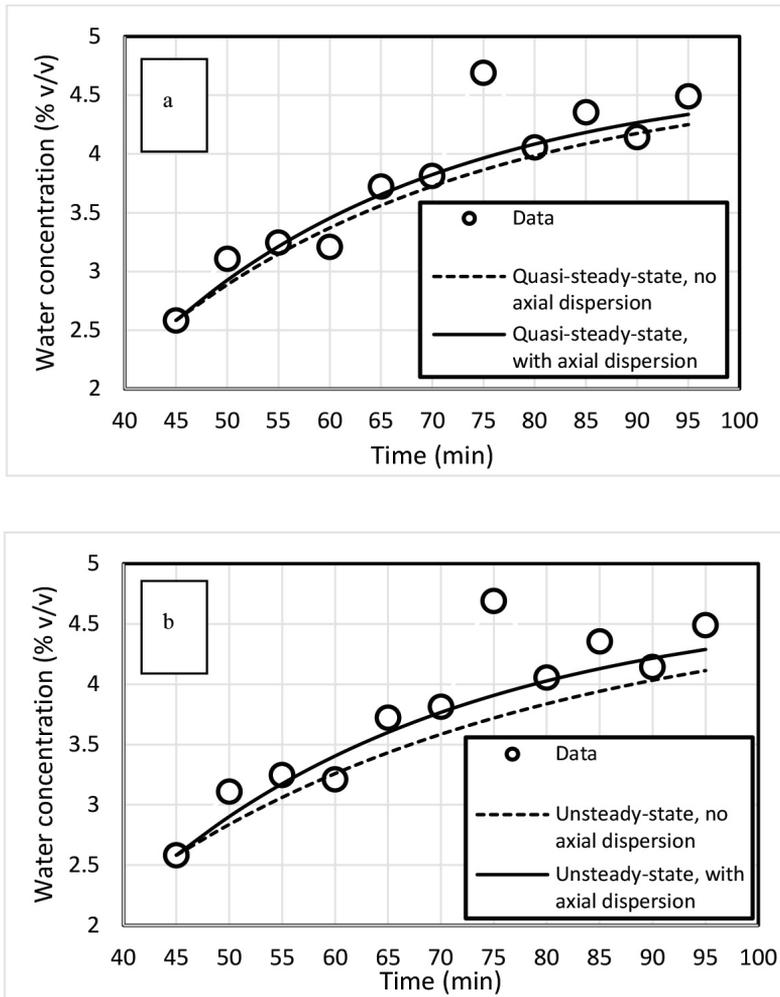
Figure 3: Comparison of water concentration in volume fraction based on the experimental measurements and calculation of various AD models using synthetic zeolite as adsorbent with assumption in quasi-steady-state: (a) as well as unsteady-state; (b) at conditions: heating temperature of 170°C, pressure of 1 atm and condensate flows of 2.38 ml min^{-1}.

4. CONCLUSION

Ethanol could be purified using AD method with natural and synthetic zeolites as adsorbent at 1 atm of pressure. The designed AD equipment and both types of used adsorbent could increase ethanol concentration. The process of AD can

be quantitatively described by several models, such as quasi-steady-state with no axial dispersion (Model 1), unsteady-state with no axial dispersion (Model 2), quasi-steady-state with axial dispersion (Model 3) and unsteady-state with axial dispersion (Model 4). All models can describe adsorption mechanism well. Highest ethanol concentration achieved by using natural zeolite, 19.64 g and 15.39 g synthetic zeolite is about 96.96 v/v, 96.88 v/v and 97.472% v/v. This concentration is above the azeotropic concentration. Thus, AD with natural and synthetic zelolites as adsorbent shows good performance and success in passing the azeotropic point.

5.   ACKNOWLEDGEMENTS

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