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Modeling of Fixed Adsorptive Distillation in Batch Operation

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Abstract: This paper presents the modeling of fixed adsorptive distillation in batch operation. A combination of theoretical and empirical approaches is used to derive the model with the following procedures:

(i) modeling through each sub-unit based on ideal concepts and assumptions,
(ii) addition of empirical correction factors into the model to eliminate assumptions.

The model is designated to predict the model parameter, which is the composition of the second column product, as a function of three process variables (i.e. time, feed composition, and flow ratio). It is found that the two above–mentioned approaches result in a representative model with an average error percentage of 5.46%.

Keywords: Modeling, fixed adsorptive distillation, batch operation, unit - sub-unit, empirical correction factors

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INTRODUCTION

A state of art of technology, a so-called fixed adsorptive distillation (FAD), to enhance the distillation of azeotropic solution of isopropanol (IPA)-water mixtures has been developed. FAD was a hybrid process, combining two conventional separation techniques including distillation and adsorption; the principal, approach and advantages of FAD have been discussed in (1). From the experimental point of view, FAD was proved to be able to break up the azeotropic point existing in the IPA-water mixtures. Even though FAD was originally carried out to handle a homogeneous minimum boiling azeotrope, a modification of types of adsorbent and recycle system is convinced to be able to perform the separation of general homogeneous azeotropes as well.

With respect to reduce the experimental works and for the purpose of design applications such as simulation and scale-up, a mathematical model to describe the FAD process must be established. This paper aims to develop the FAD model especially to handle the azeotropic solution of IPA-water mixtures in batch operation (dynamic behavior of the FAD process). A batch FAD process can be indicated from the flow pattern in the way of how the feed and the product are conducted. There is no fresh feed fed into the first column and no products taken out from the bottom sides of the two columns during the process. Many literatures (2–4) have presented the examples of modeling of applied engineering problems; as well, modeling related to distillation process or adsorption phenomena has been reported in some papers (5–11). However, most deal with a single system (device) and the model is both derived and solved theoretically using either analytical or numerical methods. In FAD, three systems or sub-units with a recycle stream are existing, as shown in Fig. 1; it causes the derivation of the FAD model to become more complex. In this work, two approaches of procedures which were a combination of the theoretical and the empirical aspects were tried to use in the arrangement of the model, i.e.:

(i) derivation of model based on some pertinent ideal concepts and assumptions through each sub-unit followed by substitutions to constitute the whole FAD model; and
(ii) validation of the model by adding empirical correction factors to eliminate assumptions (simplifications).

First of all, the model is derived theoretically until differential equations are obtained. Rather, analytical integration with simplifications is enforced to find out the ultimate FAD model. This non-exact (approximate) solution is then corrected with the addition of empirical correction factors. By these approaches, the model may be valid for certain conditions only; in order that the model can be applied for other operating conditions, it just requires a modification of empirical correction factors.

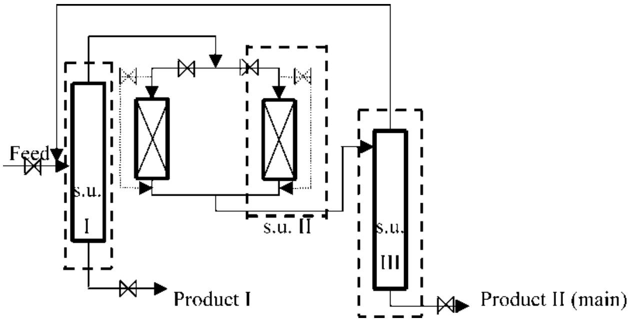


Figure 1. Three sub-units (s.u.; distillation-adsorption-distillation) which compose the unit of FAD. ⋈ = Feed entrance is opened when the fresh feed is fed at initial process and closed during operation; product extrance is opened after a certain operating time (end of operation).

According to the above procedures, there will be three sub-unit models; these models are then re-combined by substitutions to constitute the representative model of the FAD process. Even though the derivation of the model is executed through each sub-unit, all streams from other sub-units which get involved surrounding a sub-unit are not neglected. The ultimate model is designated to determine the model parameter, which is the composition of the second column product (bottom side), as a function of three process variables including operating time, feed composition of column I, and the ratio of flow surrounding the adsorbent bed. Once the ideal FAD model is established and qualitatively shows consistency with the experimental results, some empirical correction factors are then added into the model to correct the assumptions. The empirical correction factors are obtained by optimization of these variables with respect to minimizing the difference of the model parameter values between the proposed model and the experimental data. These differences, which can be expressed in terms of error percentage, also become a justification tool of the model validity in which the lower the error percentage is, the more valid the model is. Finally, the corrected model is applied to perform some simulations especially with respect to defining the optimum operating condition of the second column performance.

THE DEVELOPMENT OF THE MODEL

Theoretically, the model of FAD can be formulated by taking into account all the physicochemical phenomena which get involved in the process such as mass balance, equilibrium, and rate process. The tool of energy balance is not used especially in the modeling of the distillation column because the mass balance and equilibrium tools are deemed to be sufficient to build the representative model of this part. Some complexities that may arise and be difficult to be expressed quantitatively are simplified by considering the following assumptions: the liquid and vapor in both distillation columns are in equilibrium state; column I of distillation operates below the azeotropic point; column II operates above the azeotropic point; the holdup liquid in the distillation column and bed of adsorbent is neglected; the adsorbent (silica gel) adsorbs water only (single-component adsorption); constant flow rate; and constant density (average molecular weight) of IPA-water mixtures.

As reported previously, there are three separation zones applied in the FAD, i.e. distillation-adsorption-distillation. The two packed columns of distillation are intrinsically similar to the conventional ones, so a concept of HETP (Height Equivalent to a Theoretical Plate) can be used to characterize the performance of the column (12, 13). In the adsorption zone, in order to predict the life time of the adsorption process as an anticipation of the saturated condition, the mechanism of an adsorbed component (solute) from the bulk fluid (liquid) onto the surface of the adsorbent must be known. Generally speaking, the adsorption frequently takes place on the inner (internal) surface of the porous adsorbent; to reach this part, a solute will undergo the following series of steps (2):

(i) mass transfer from the bulk fluid to the external surface;
(ii) diffusion from the external surface through the pore;
(iii) mass transfer from the bulk fluid in the pore to the wall of pore or internal surface; and
(iv) adsorption onto the internal surface.

In principle, a rigorous model of the adsorption rate can be developed by taking into account all of the above mechanisms. However, in most cases, the steps c and d occur quite fast compared to steps a and b hence the rate of adsorption process is usually controlled by a or b, or both a and b. In a special case, when the size of the adsorbent is very small (typically less than 3 mm), like in this FAD's experiments, step b will be going relatively fast, thus step a becomes the determining rate of the whole adsorption process. Some assumptions and basic concepts pertaining to distillation and adsorption above will be applied in the development of the following FAD model.

From Fig. 1 the split of FAD unit gives the following three sub-units which are attached with some necessary mathematical variables that will show up in the FAD model (Fig. 2).

In batch operation, the composition of the second column product changes subject to the changes of those around the first distillation column and bed of adsorbent. These composition changes can be traced by modeling through each sub-unit as the following steps,

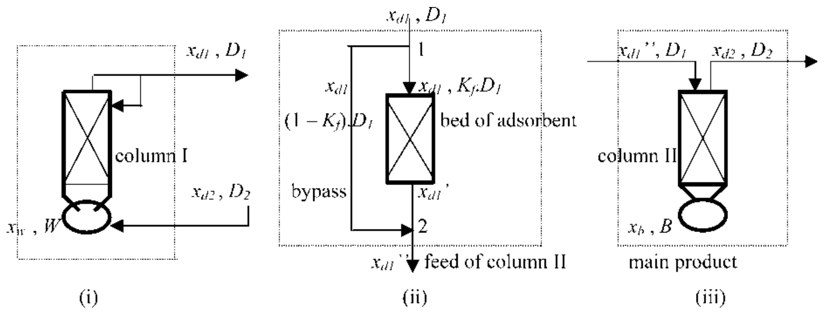


Figure 2. The split of FAD unit into three sub-units: sub-unit of distillation column I (i), sub-unit of bed of adsorbent (ii), and sub-unit of distillation column II (iii).

Sub-unit I (Column I)

The model of sub-unit I especially reveals the changes in composition of feed and products (top and bottom) of column I during the batch FAD process. From Fig. 2, the total mass balance around column I by neglecting the holdup liquid in the column can be arranged as follows,

$$D_2 - D_1 = \frac{dW}{dt} \tag{1}$$

Analogously, the mass balance of species of IPA,

$$x_{d2}D_2 - x_{d1}D_1 = \frac{d(x_w W)}{dt} \tag{2}$$

The correlation of x_{d1} versus x_w can be determined graphically from the liquid-vapor equilibrium (LVE) curve of IPA-water system under the azeotropic point, and is affected by the number of equilibrium stage and reflux ratio operated in the distillation column. In this model, however, an empirical equation to correlate x_{d1} versus x_w based on the given operating conditions is preferred to use to avoid using manual drawing. In case of the IPA-water separation system distilled in three equilibrium stages and total reflux, the empirical equation smoothly follows the third-order polynomial form.

$$x_w = f(x_{d1}) = \alpha x_{d1}^3 + \beta x_{d1}^2 + \gamma x_{d1} + \delta$$

or

$$x_{d1} = f(x_w) = a x_w^3 + b x_w^2 + c x_w + d \tag{3}$$

In addition, an empirical expression shown in Eqn. (3) may also be valid for any other conditions because most curve-graph follows this form smoothly.

Sub-unit II (Bed of Adsorbent)

In order to know the changes in composition of IPA-water mixtures exiting the bed of adsorbent as well as entering the second distillation column during the process, a model of sub-unit II must be defined. These compositions depend on the adsorption rate where some amount of water adsorbed on the adsorbent as well as the flow ratio surrounding the bed of adsorbent. In simply, the amount of water (*A*) adsorbed onto the adsorbent can be calculated using Eqn. (4).

$$n_{A,adsorbed} = (C_{Ain} - C_{Aout})F \tag{4}$$

In order that the composition of IPA shows up in the equation, Eqn. (4) can also be expressed in term of mole fraction of IPA,

$$n_{A,adsorbed} = \left[(1 - x_{d1}) - \left(1 - x'_{d1}\right)\right]K_f D_1 \tag{5}$$

where

$$x'_{d1} = 1 - \frac{C_{Aout}F}{K_f D_1} \tag{6}$$

The composition of IPA entering column II is evaluated from the mass balance of IPA around the mixing zone (point 2 of Fig. 2).

$$x'_{d1}K_f D_1 + x_{d1}(1 - K_f)D_1 = x''_{d1}D_1$$

or,

$$x''_{d1} = x'_{d1}K_f + x_{d1}\left(1 - K_f\right) \tag{7}$$

The value of C_{Ain} in Eqn. (4) depends on the composition of distillate produced by the first distillation column. To determine the value of C_{Aout}, a correlation of C_A as a function of position in bed (z) and time (t) is needed. By arranging the mass balance on species of water in the liquid phase and on the solid (adsorbent) at the volume element of the bed of adsorbent as shown in Fig. 3, will give equations $C_A = f(z, t)$.

The mass balance of water across the bed of adsorbent is affected by the adsorption rate and the flow of liquid through the adsorbent. Because of the

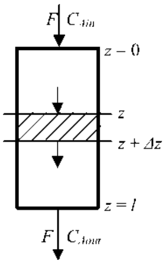


Figure 3. The mass balance of species *A* (water) at volume element of the bed of adsorbent.

small size of adsorbent used in this FAD's experiment, the determining rate of the adsorption process is controlled by the mass transfer from the bulk fluid to the external surface and can be defined as follows (2, 14),

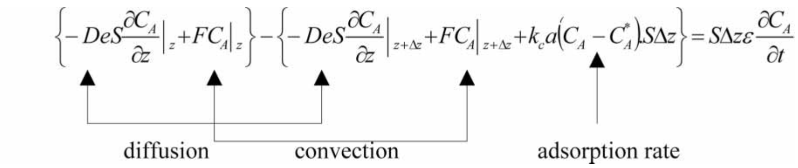
$$N_A\left(\frac{molA}{time \cdot volume}\right) = k_c a\left(C_A - C_A^*\right) \tag{8}$$

C_A^* that represents the concentration of water in the liquid phase which is in equilibrium with that on the adsorbent, is assumed to follow Henry's law.

$$C_A^* = HX_A \tag{9}$$

The flow of liquid across the pores of the adsorbent is driven due to two simultaneous mass transfer mechanisms, i.e. diffusion and convection; so, applying Eqn. (8) into the mass balance of A in the liquid phase,

Rate of Input – Rate of Output = Rate of Accumulation



$$\left\{-DeS\frac{\partial C_A}{\partial z}\Big|_z + FC_A\Big|_z\right\} - \left\{-DeS\frac{\partial C_A}{\partial z}\Big|_{z+\Delta z} + FC_A\Big|_{z+\Delta z} + k_c a\left(C_A - C_A^*\right)S\Delta z\right\} = S\Delta z\varepsilon\frac{\partial C_A}{\partial t}$$

$$\frac{(\partial C_A/\partial z)\big|_{z+\Delta z} - (\partial C_A/\partial z)\big|_z}{\Delta z} - \frac{F}{SDe}\left(\frac{C_A\big|_{z+\Delta z} - C_A\big|_z}{\Delta z}\right) - \frac{k_c a}{De}\left(C_A - C_A^*\right) = \frac{\varepsilon}{De}\frac{\partial C_A}{\partial t}$$

If Δz approaches to zero,

$$\frac{\partial^2 C_A}{\partial z^2} - \frac{F}{SDe}\frac{\partial C_A}{\partial z} - \frac{k_c a}{De}\left(C_A - C_A^*\right) = \frac{\varepsilon}{De}\frac{\partial C_A}{\partial t} \tag{10}$$

If the diffusion towards the axial direction is ignored due to the dominant contribution of the convective flow, Eqn. (10) becomes simpler,

$$-\frac{F}{S}\frac{\partial C_A}{\partial z} - k_c a \cdot \left(C_A - C_A^*\right) = \varepsilon\frac{\partial C_A}{\partial t} \tag{11}$$

By the same token, the mass balance of A on the adsorbent at the volume element of bed can be defined,

$$\frac{\partial X_A}{\partial t} = \frac{k_c \cdot a}{\rho_b}\left(C_A - C_A^*\right) \tag{12}$$

There are two simultaneous differential Eqns. (11) and (12) and one additional Eqn. (9) to determine the concentration of water at any position and time in the bed of adsorbent. In particular to find out the value of C_{Aout}, it is obtained by solving the above equations for the position z equals to l (length of bed).

Sub-unit III (Column II)

Similarly to sub-unit I, the mass balance around sub-unit III can be defined,

$$D_1 - D_2 = \frac{dB}{dt} \tag{13}$$

$$x''_{d1} D_1 - x_{d2} D_2 = \frac{d(x_b B)}{dt} \tag{14}$$

The correlation x_{d2} versus x_b is analogous to that in column I, but above the azeotropic point. All the three sub-unit models together with the supporting equations have been formulated (Eqns. (1)–(14)); in order to find out a simpler model describing the composition of the second column product as a function of process variables of the first distillation column and bed of adsorbent, some substitutions among these models are needed. Substituting Eqn. (14) into Eqn. (2) will yield Eqn. (15).

$$x''_{d1} D_1 - \frac{d(x_w W)}{dt} = x_{d1} D_1 + \frac{d(x_b B)}{dt} \tag{15}$$

Eqns. (6) and (7) are then substituted into Eqn. (15) and be modified to give Eqn. (16).

$$d(x_b B) = \left[K_f (1 - x_{d1}) - \frac{C_{Aout} F}{D_1} \right] D_1 dt - d(x_w W) \tag{16}$$

Eqn. (16) seems quite complicated to solve analytically since a batch FAD gives a consequence of dynamic condition in which the composition of distillate (x_{d1}) will change as a function of time and directly affect the composition of water exiting from the bed of the adsorbent (C_{Aout}) as well. It is expected that x_{d1} always approaches the azeotropic point as an attempt to achieve the successful FAD. If the feed composition of column I is kept close to the azeotropic point, x_{d1} will be relatively the same (i.e. slightly below the azeotropic point) during the operation so that it can be considered to be constant. In this paper, another simplification is also used that the value of C_{Aout} which essentially varies with time is determined separately, given from the solution of Eqns. (9), (11), and (12); then, the integration of Eqn. (16) become simpler.

$$\int_{x_{bo} \cdot B_o}^{x_b \cdot B} d(x_b B) = \int_0^t \left[K_f (1 - x_{d1}) - \frac{C_{Aout} F}{D_1} \right] D_1 dt - \int_{x_{wo} \cdot W_o}^{x_w \cdot W} d(x_w W)$$

$$x_b B = \left[K_f (1 - x_{d1}) - \frac{C_{Aout} F}{D_1} \right] D_1 t + x_{wo} W_o - x_w W$$

$$x_b = \frac{[K_f (1 - x_{d1}) - (C_{Aout} F / D_1)] D_1 t + x_{wo} W_o - x_w W}{B} \tag{17}$$

Eqn. (17) will be more useful if W and B are also expressed in term of time. Integration of Eqns. (1) and (13) with initial B (B_o) equals to zero, and then be substituted into Eqn. (17) gives,

$$x_b = \frac{\left[K_f(1 - x_{d1}) - (C_{Aout}F/D_1)\right]D_1 t + x_{wo}W_o - [W_o + (D_2 - D_1)\cdot t]x_w}{(D_1 - D_2)\cdot t}$$

or

$$x_b = \left[K_f(1 - x_{d1}) - \frac{C_{Aout}F}{D_1}\right]\frac{D_1}{(D_1 - D_2)} + \frac{W_o x_{wo}}{(D_1 - D_2)\,.\,t} + \left[1 - \frac{W_o}{(D_1 - D_2)\cdot t}\right]x_w \tag{18}$$

To reduce number of variables, x_{d1} can be stated in term of x_w, and vice versa; substitution of Eqn. (3) into (18) gives,

$$x_b = \left[K_f(1 - x_{d1}) - \frac{C_{Aout}F}{D_1}\right]\frac{D_1}{(D_1 - D_2)} + \frac{W_o x_{wo}}{(D_1 - D_2)\cdot t} + \left[1 - \frac{W_o}{(D_1 - D_2)\cdot t}\right]\cdot\left(\alpha x_{d1}^3 + \beta x_{d1}^2 + \gamma x_{d1} + \delta\right)$$

or

$$x_b = \left\{K_f\left[1 - \left(a x_w^3 + b x_w^2 + c x_w + d\right)\right] - \frac{C_{Aout}F}{D_1}\right\}\frac{D_1}{(D_1 - D_2)} + \frac{W_o\,x_{wo}}{(D_1 - D_2)\cdot t} + \left[1 - \frac{W_o}{(D_1 - D_2)\cdot t}\right]x_w \tag{19}$$

Finally, Eqn. (19) is the primary mathematical models proposed to represent a batch FAD process for separation of IPA-water mixtures; the detailed FAD model for separation system studied in this work is summarized in the following Table 1.

EXPERIMENTAL PART

In general cases of batch distillation, the initial conditions including the amount of feed of column I (W_o) and its composition (x_{wo}) are known or fixed by the previous process, whereas the flow of streams (D_1, D_2, and F) including reflux ratios of both columns in this FAD process essentially can be stated as design variables so that the composition of the second product (x_b) can be calculated. Three parts of experimental works have been conducted in the previous work i.e.: FAD experiments, equilibrium sorption, and adsorption through fixed bed of adsorbent. The FAD experiments have recorded the effect of three process variables (time, feed composition of column I, and flow ratio) to the composition

Table 1. Detailed model of FAD process for separation of IPA-water mixtures in batch operation

Model/equation		Model parameter	Process variable
Primary model:		Composition of the second column product (x_b)	Time (t)
$x_b = \left[K_f(1 - x_{d1}) - \frac{C_{Aout}F}{D_1}\right]\frac{D_1}{(D_1 - D_2)} + \frac{W_o x_{wo}}{(D_1 - D_2)\cdot t} + \left[1 - \frac{W_o}{(D_1 - D_2)\cdot t}\right]\cdot(\alpha x_{d1}^3 + \beta x_{d1}^2 + \gamma x_{d1} + \delta)$ or $x_b = \left\{K_f\,[1 - (ax_w^3 + bx_w^2 + cx_w + d)] - \frac{C_{Aout}F}{D_1}\right\}\frac{D_1}{(D_1 - D_2)} + \frac{W_o x_{wo}}{(D_1 - D_2)\cdot t} + \left[1 - \frac{W_o}{(D_1 - D_2)\cdot t}\right]x_w$	Eqn. (19)		Feed composition (x_{wo}) flow ratio (K_f)
Supporting models:		Concentration of water exiting the bed of adsorbent (C_{Aout} or C_A at $z = l$)	Initial and boundary conditions of C_A and X_A
$-\frac{F}{S}\frac{\partial C_A}{\partial z} - k_c a\cdot(C_A - C_A^*) = \varepsilon\frac{\partial C_A}{\partial t}$	Eqn. (11)		
$C_A{}^* = HX_A$	Eqn. (9)		
$\frac{\partial X_A}{\partial t} = \frac{k_c\cdot a}{\rho_b}(C_A - C_A^*)$	Eqn. (12)		

of the second column product as reported in (1) and some will be presented again in the next Table 3. In this work, these data are used as a benchmark where the model parameter from the model calculations must refer to; in other words, these data are used to validate the model in which the empirical correction factors will be defined and put into the model. Two coefficients required in the calculation of this model, i.e. the equilibrium constant of Henry (H) and volumetric mass transfer coefficient ($k_c a$) were obtained experimentally in the separated experiments (i.e. equilibrium sorption and adsorption through fixed bed of adsorbent) and found to be 2.3×10^{-2} mol/mL and 8.7×10^{-3} min $^{-1}$, respectively. These two coefficients were evaluated at 80°C, the temperature at which the adsorption process underwent was approximately the equilibrium temperature of IPA-water mixtures at azeotropic composition. The FAD experiments worked on 278 mL of feed of column I, and 4.9, 1.05, and 4.4 mL/min of the flow streams of D_1, D_2, and F, respectively ($K_f = 0.898$) for variation of feed composition. The packing used was a raschig ring shape with a measurement of $1/4 \times 1/4$ in; the value of HETP has a range of 0.1–0.6 ft (12). Using the average value of HETP (0.35 ft = 10.67 cm), the 32.1 cm-height of column I will give three theoretical equilibrium stages. The data of LVE of IPA-water mixtures at atmospheric pressure are given in Table A1 and Fig. A1 in the Appendix. The mass of adsorbent used was 36.474 g filled in a 10.1–2.4 cm of length and diameter of the adsorbent bed. Beside the second column product, the experimental works also took out samples from the bottom side of the first column to be analyzed at certain intervals of time, hence the data of x_w were available as well (Figure A2).

DISCUSSION AND SIMULATION

From the qualitative point of view, Eqn. (19) implies that the composition of the second column product (x_b) in a batch FAD operation is obviously affected by the flow ratio of adsorptive and by-pass flow which is expressed in terms of flow fraction (K_f), operating time (t) and the initial feed composition of column I (x_{wo}). The effect of the flow ratio is not questioned because the more distillate flown through the adsorbent (high K_f) will raise the composition of the second column product. By the same token, noticing the third term in Eqn. (19), the composition of the second column product can also be enhanced by increasing the (initial) feed composition of column I. It seems there might be an optimum operating condition dealing with the composition of the first column distillate which is directly affected by feed composition, that the higher value of x_{d1} will actually reduce the value of the first term in Eqn. (19) but increase the value of the last term. However, considering the value of the second term which represents the performance of the adsorption process can confirm as to what kind of profile of the second column product's composition will be as an effect of the composition of the first column distillate. The higher composition of the distillate will have less content of water so that the value of the second term will be low as well due to the low concentration of water (C_{Aout}), and vice versa; so, eventually, the effect of the composition of the first column distillate is in agreement with that of the feed composition. As a batch process, the composition of the second column product will also be dependent on operating time. Unlike in the single conventional batch distillation operated at a constant reflux ratio, the profile of the product's composition in the batch FAD does not decrease sharply as the time increases. As shown in the model, the existence of operating time as denominator in two places with opposite signs (addition and subtraction) may change the composition just a little bit, then decrease smoothly when the rate of adsorption becomes lower (higher C_{Aout}), and finally relatively constant at infinite time.

These qualitative assessments seem to be in accordance with the experimental data reported in (1). The next procedure is validation of the model by adding some empirical correction factors into the model to correct the assumptions which are actually difficult to achieve in real phenomena. The model is validated with the experimental data of FAD as mentioned in the section on the experimental part, particularly for variations of feed composition because most data are well available. The determination of C_{Aout} that involves partial differential equation is solved numerically using finite difference approximation principles (explicit method) in which these differential equations are converted into algebraic equations (Table A.2 Appendix), and then programmed in Visual Basic language. The values of x_{d1} model are calculated based on the given data of x_w using an empirical relationship on three equilibrium stages and total reflux ratio, and these values will determine the concentration of water entering the bed of the adsorbent (C_{Ain}). Subsequently, these C_{Ain} data are used as initial conditions to define C_{Aout} at various operating time. Since the assumptions taken into account in the derivation of the model are closely related to some theories in distillation and adsorption, ideally there should be three empirical correction factors put on three different places in the model representing the three sub-units. However, because the proposed model does not require the LVE data of the second distillation column (from Eqn. (19), only two empirical correction factors (i.e. C_{F1} and C_{F2}) are added and attached especially on the terms which have complex characters and indicate the performances of the first distillation column and adsorbent bed or combination of both. To make sure the empirical correction factors have been put on the most appropriate place in the model, all possibilities are tried and those which give the most similar empirical correction factors resulted among the given data (variations of feed compositions of column I) are chosen. The values of C_{F1} and C_{F2} are determined by optimization of these variables with respect to the result the minimum value of the sum of squared errors; this error represents the difference between the composition calculated from the proposed model and that from experimental measurements. The optimization calculations were also carried out using a numerical solution (i.e.

Hooke Jeeves method), and found out the average values of C_{F1} and C_{F2} to be 0.3071 and 0.9163, respectively. As a matter of fact, the values of empirical correction factors actually vary a little bit subject to the feed composition; detailed empirical correction factors and their applications are given in Table 2.

By using the average value of empirical correction factors, the corrected form of batch FAD model for separation of IPA-water mixtures on three equilibrium stages of column I is as follows,

$$\begin{aligned} x_b = 0.3071\Big\{&K_f[1-(0.275x_w^3-0.2317x_w^2+0.1012x_w+0.6206)] \\ &-\frac{C_{Aout}F}{D_1}\Big\}\frac{D_1}{(D_1-D_2)}+\frac{W_o x_{wo}}{(D_1-D_2)\cdot t} \\ &+0.9163\left[1-\frac{W_o}{(D_1-D_2)\cdot t}\right]x_w \end{aligned} \tag{20}$$

Table 3 and Fig. 4 show the composition of the second column product as a function of operating time and feed composition based on the experimental measurements and model calculations.

From Table 3 and Fig. 4, it can be seen that the proposed model derived using the two approaches of procedures tried in this work can describe well

Table 2. Detailed empirical correction factors and their applications

Model form:

$$x_b = C_{f1}\left\{K_f[1-(ax_w^3+bx_w^2+cx_w+d)]-\frac{C_{Aout}F}{D_1}\right\}\frac{D_1}{(D_1-D_2)}+\frac{W_o x_{wo}}{(D_1-D_2)\cdot t}$$
$$+\,C_{f2}\left[1-\frac{W_o}{(D_1-D_2)\cdot t}\right]x_w$$

Empirical correction factor	Operating Conditions in Application (3 equilibrium stages; nearly total reflux; flow ratio = 8.80 ($K_f = 0.898$))
$C_{f1} = 0.5954$	Feed composition = around 87 wt.% of IPA
$C_{f2} = 0.8023$	
$C_{fl} = 0.4384$	Feed composition = around 85 wt.% of IPA
$C_{f2} = 0.9398$	
$C_{f1} = 0.3626$	Feed composition = around 80 wt.% of IPA
$C_{f2} = 0.7063$	
$C_{fl} = 0.5418$	Feed composition = around 70 wt.% of IPA
$C_{f2} = 0.8818$	
$C_{f1} = 0.0188$	Feed composition = around 60 wt.% of IPA
$C_{f2} = 1.1262$	

Note: The average value is evaluated from the lowest and the highest value

Table 3. The comparison of the composition (purity) of the second column product in mole fraction based on the Experimental data and calculations of FAD model at the flow ratio of 8.80 ($K_f = 0.898$) and various feed compositions of column I (coded with notations a, b, c, d, e)

Time, min	x_w Data	x_b Data	x_{dl} Model	C_{Aout} Model	x_b Model	% Error of x_b
25	—[a]	—[a]	—	—	—	—
	0.6403[b]	0.8066[b]	0.6626	0.005461	0.8529	5.74
	0.7143[c]	0.7586[c]	0.6749	0.005197	0.7722	1.80
	0.4500[d]	0.6238[d]	0.6443	0.005868	0.6587	5.60
	0.2617[e]	0.3387[e]	0.6361	0.006054	0.3465	2.31
30	0.8751	0.8373	0.7160	0.004346	0.8178	2.33
	0.6613	0.7845	0.6657	0.005380	0.8095	3.18
	0.6912	0.8479	0.6707	0.005273	0.7744	8.67
	0.4827	0.6292	0.6464	0.005806	0.6094	3.15
	0.2540	0.3750	0.6359	0.006045	0.3514	6.30
35	0.7518	0.9301	0.6826	0.004992	0.9559	2.78
	0.7679	0.7870	0.6862	0.004917	0.6896	12.38
	0.6536	0.7100	0.6646	0.005373	0.7834	10.34
	0.4813	0.6025	0.6463	0.005774	0.6153	2.12
	0.2555	0.3594	0.6359	0.006008	0.3414	5.02
40	0.8479	0.8723	0.7075	0.004426	0.8598	1.44
	0.7143	0.7609	0.6749	0.005081	0.7591	0.24
	0.6366	0.7563	0.6621	0.005351	0.7710	1.94
	0.4802	0.6632	0.6462	0.005695	0.6192	6.63
	0.1994	0.3646	0.6338	0.005974	0.3865	6.02
45	0.7073	0.8167	0.6736	0.005220	0.9523	16.61
	0.7272	0.7845	0.6774	0.005138	0.7586	3.31
	0.6274	0.7472	0.6608	0.005496	0.7550	1.04
	0.4813	0.6348	0.6463	0.005818	0.6207	2.22
	0.1905	0.2960	0.6334	0.006113	0.3755	26.84
50	0.8479	0.8723	0.7075	0.005088	0.8626	1.11
	0.7058	0.7495	0.6733	0.005880	0.7776	3.75
	0.6912	0.7207	0.6707	0.005943	0.7133	1.02
	0.4840	0.6498	0.6465	0.006541	0.6210	4.43
	0.1735	0.3534	0.6326	0.006897	0.3687	4.31
55	0.9093	0.9835	0.7278	0.005369	0.8343	15.16
	0.6220	0.7870	0.6601	0.007173	0.8124	3.23
	0.6791	0.7338	0.6686	0.006933	0.7082	3.49
	0.4114	0.6441	0.6422	0.007693	0.6449	0.12
	0.1880	0.4000	0.6333	0.007959	0.3485	12.89
60	—	—	—	—	—	—
	0.7143	0.7894	0.6749	0.006251	0.7827	0.85
	0.6771	0.7058	0.6683	0.006421	0.7010	0.68
	0.3813	0.5888	0.6408	0.007155	0.6461	9.72
	0.2052	0.3656	0.6340	0.007342	0.3338	8.71

[a] Feed of IPA of 87.2 wt.%.
[b] Feed of IPA of 85.1 wt.%.
[c] Feed of IPA of 80.4 wt.%.
[d] Feed of IPA of 70.1 wt.%.
[e] Feed of IPA of 60.0 wt.%.

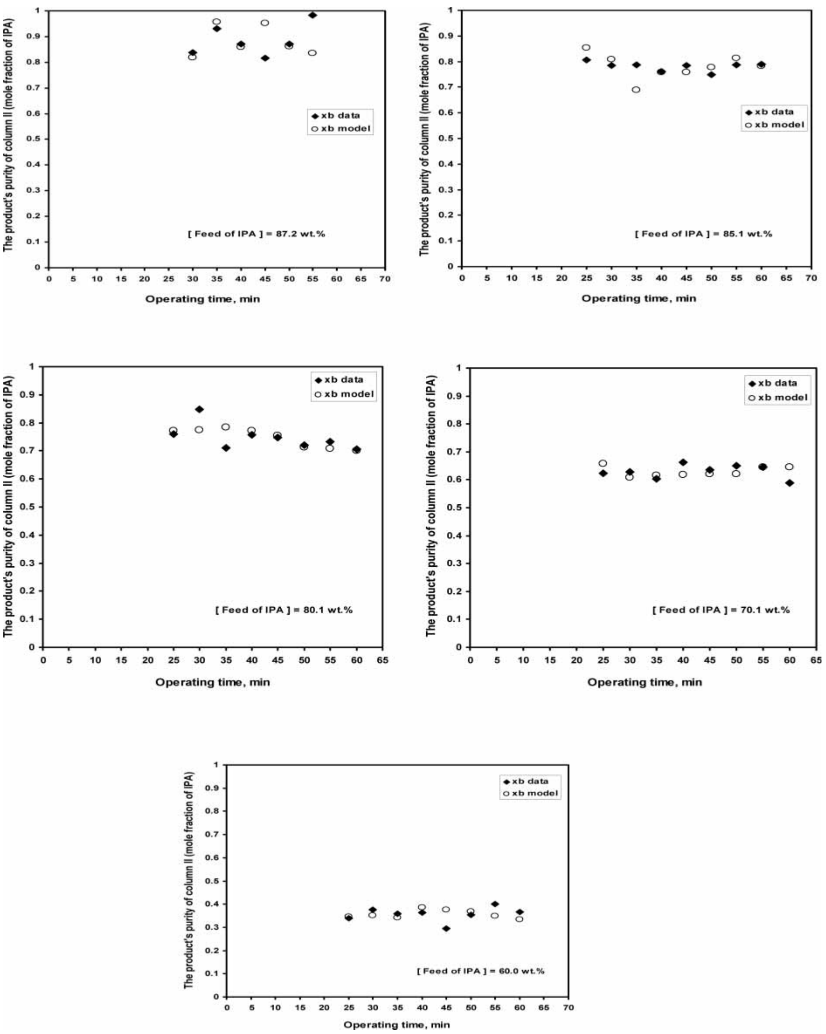


Figure 4. The comparison of the composition (purity) of the second column product in mole fraction based on the experimental measurements and calculations of FAD model at the flow ratio of 8.80 ($K_f = 0.898$) and various feed composition of column I.

the batch FAD process for separation of IPA-water mixtures in which the average error percentage for all points evaluated is 5.46%. This error percentage is considered as the only tool to asses the validity of the proposed model, because as far as the authors are concerned there has not been any software or model established for dynamic modeling of this quite new state of art of technology. In addition, it must be noticed that these deviations may happen not merely because of the less validity of the model but it might also be caused by the less accurate experimental data due to experimental errors.

As a matter of fact, Eqn. (20) is a very specific case for separation of IPA-water mixtures distilled in three equilibrium stages and nearly total reflux, so that it can not be applied for any other conditions and mixture system. However, Eqn. (19) which is more general than Eqn. (20) is eligible for separation of any homogeneous minimum boiling azeotrope in which the empirical expression to correlate the top and bottom compositions in column I follows the third-order polynomial form. Furthermore, Eqn. (18), which is more general than Eqns. (19) and (20), is considered as the model of batch FAD process for separation of any homogeneous minimum boiling azeotrope. Only empirical constants and correction factors need to be added, obtained from processing of experimental data of the system to be studied; the more experimental data are available, the more valid these empirical coefficients are.

As the purpose of establishment of the model, this model is expected to be able to use for some applications of design in the FAD process. As explained in (1), the principle of FAD method is essentially an attempt 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. In order that the composition of the second column product reaches a very high concentration or pure product, it can be achieved by enhancing the performance of the second distillation column including the treatment of reflux ratio and number of equilibrium stage. Looking at Fig. 1 and the proposed model in Eqn. (20), the performance of the second column is basically represented by the recycle stream of D_2. The less D_2 recycled means the higher reflux ratio applied in column II is, and vice versa. If it is considered as a single distillation column, it must theoretically increase the composition of the second column product. However, looking at the proposed model, there might be an optimum condition dealing with the reflux ratio operated in column II. The high reflux ratio of column II (low D_2) will give larger value of difference from D_1 taking place in both positive and negative denominators hence potentially increasing as well as decreasing the composition of the second column product. It sounds contradictive from the previous statement, but if one notices that the FAD process denotes a unit of process where the distillate of the second column is recycled to the first column instead of taken out as top product like in a single distillation, it becomes reasonable to have a different consequence. On the one side, the high reflux ratio of column II (low D_2) will improve the performance of column II as a single column; on the other side, the recycled D_2 directly affects the first column's performance in which the low D_2 will reduce the feed composition of column I as well as the first column distillate, and vice versa. Figure 5 shows the simulation of D_2 applied in a moderate feed composition (70.1 wt.%) as an effort to improve the second column's performance with respect to maximizing the product's composition in the FAD process. In this simulation, the effect of D_2 to the composition of the second column product is simulated by varying the values of D_2 as well as

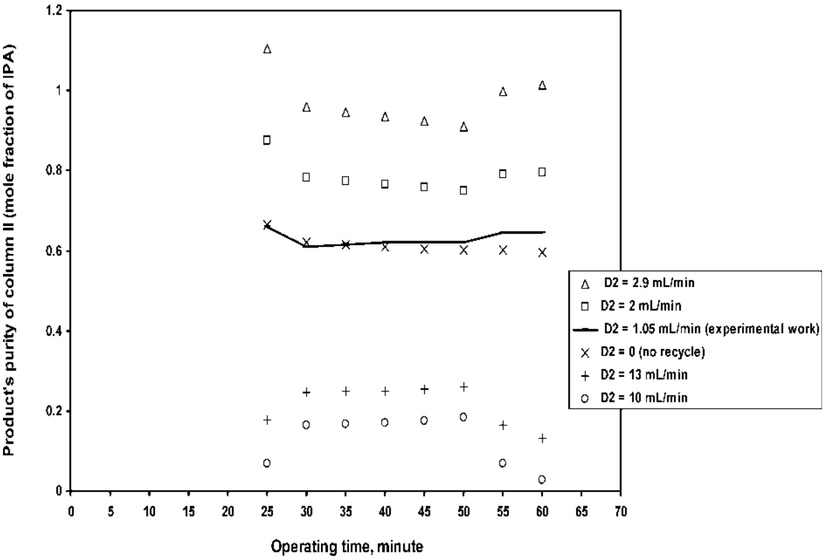


Figure 5. The simulation of values of recycle stream (D_2) with respect to improve the second column's performance to achieve the best composition (purity) of the second column product.

D_1 while other values of process variables are considered the same as those given in the section on the experimental part.

Figure 5 confirms that there is an optimum condition dealing with the reflux ratio operated in column II. An increase of D_2 at the range from zero (without recycle) towards the value of D_1 (up to 2.9 mL/min), the product's composition of column II also increases up to pure product; however, when D_2 is higher and far from D_1 (10 and 13 mL/min), the product's composition becomes lower. Briefly speaking, the proposed model reveals that in order to achieve the highest composition of the second column product, it is recommended to operate the flow of D_1 and D_2 in similar flow rates.

FUTURE WORK

By the first procedure, the current FAD model is developed based on some ideal concepts and assumptions; in order that the model meets the best accordance to the experimental results without the addition of empirical correction factors, it requires the establishment of concepts that reflect the real phenomena undergoing in the process to eliminate the assumptions. The development of multi-adsorption theory such as in (15) where two or more solutes adsorbed onto the adsorbent is considered as one of the important parts that need to be studied intensively. In this way, the amount of each component captured by the adsorbent can be accurately evaluated; subsequently, the composition of mixture coming out from the adsorbent bed can be well predicted. As well, since the temperature may change along each sub-unit, the utilization of energy balance tool is also convinced to be able to corroborate the accuracy of the model.

CONCLUSIONS

The two approaches of procedures used in this work did well in establishing the model of batch FAD process for separation of IPA-water mixtures. The model derived based on ideal concepts and assumptions is qualitatively well justified that it has a good agreement to the experimental results in which the higher the feed composition of column I and flow ratio surrounding the bed of adsorbent are, the higher the composition of the second column product is. Quantitatively, the addition of empirical correction factors is able to minimize the deviations of model parameter (i.e. the product's composition of column II) between the model and experimental data at a level of acceptable model (around 5%). Although the model may be valid for certain conditions only, the utilization of the theoretical approach in the first procedure enables the model to be applied for any other conditions and general homogeneous minimum-boiling azeotrope separation; only the empirical values may vary depending on the operating conditions and solution system to be separated. The model also provides a specific parameter related to the improvement of the second column performance, so-called recycle stream (D_2). In order to maximize the product composition, the adjustment of reflux ratio in column II can be performed by setting the value of D_2. It is found that there is an optimum condition dealing with the reflux ratio of column II, and the model recommends D_1 and D_2 to be operated in similar flow rates.

NOMENCLATURE

a, b, c, d	empirical constants in the relationship of x_{d1} versus x_w
B	amount of liquid in the bottom of column II, mol
C_A	concentration of A (water) in liquid, mol/mL
C_A^*	concentration of A at equilibrium to that on the surface of adsorbent, mol/mL
C_{Ain}, C_{Aout}	concentration of A entering the bed of adsorbent, exiting from the bed of adsorbent, mol/mL
C_{F1}, C_{F2}	empirical correction factor of first distillation zone, adsorption zone
D_1, D_2	amount of distillate from the column I, column II, mol/min

F	volumetric rate of feed entering the bed of adsorbent, mL/min
H	equilibrium constant of Henry, mol/mL
K_f	fraction of flow (mole) passed through the bed of adsorbent
$k_c a$	volumetric mass transfer coefficient, min^{-1}
l	length of adsorbent in the bed, cm
$n_{A,\ adsorbed}$	amount of A adsorbed onto adsorbent, mol/min
N_A	rate of mass transfer of A, mol/min.cm^3
S	cross area of bed of adsorbent, cm^2
t	time, min
W, W_o	amount of liquid in the bottom of column I, initial, mol
X_A	concentration of A on the surface of adsorbent, g A/g adsorbent
x_{az}	mol fraction of IPA at azeotropic point
x_b, x_w, x_{wo}	mole fraction of IPA in the bottom of column II, I, initial I
x_d, x_{d1}, x_{d2}	mole fraction of IPA in distillate, column I, column II
x'_{d1}, x'_{d1}	mole fraction of IPA exiting from bed, feed of column II
z	position of adsorbent in the bed, cm

Greek Symbols

α, β, γ, δ	empirical constants in the relationship of x_w versus x_{d1}
ε	porosity of bed of adsorbent
ρ_b	bulk density of adsorbent (silica gel), g/cm^3

Subscripts

A	component of water
$1, 2$	column I, column II

Table A1. Data of liquid-vapor equilibrium of IPA-water mixtures at 1 atm (16)

x	y	x	y
0.0	0.0	0.3752	0.5615
0.0045	0.0815	0.4720	0.5860
0.0069	0.1405	0.4756	0.5886
0.0127	0.2185	0.5197	0.6033
0.0357	0.3692	0.5945	0.6330
0.0678	0.4647	0.7880	0.7546
0.1330	0.5036	0.8020	0.7680
0.1651	0.5153	0.9303	0.9010
0.3204	0.5456	0.9660	0.9525
0.3336	0.5489	1.0	1.0

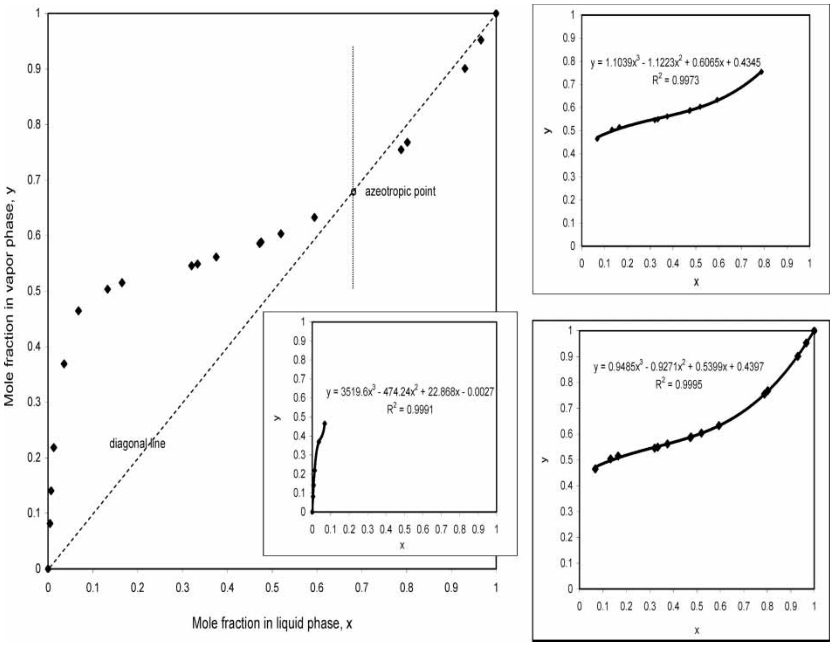


Figure A1. Liquid-vapor equilibrium (LVE) graph of IPA-water mixtures at atmosphere.

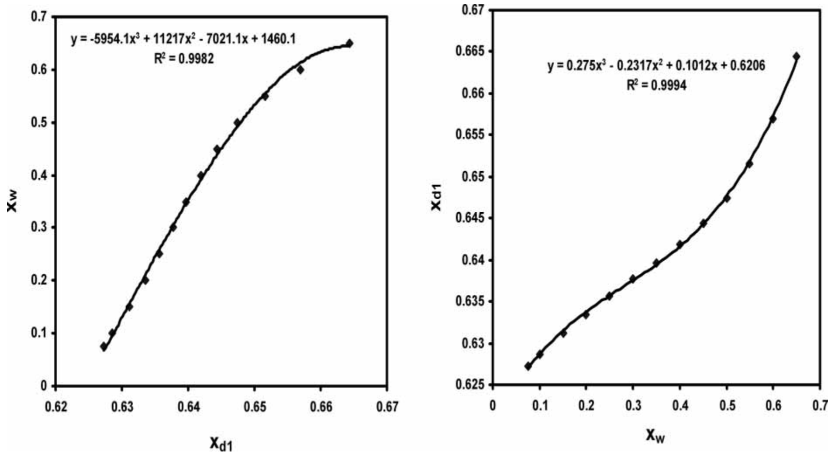


Figure A2. Empirical correlation between x_w vs x_{dI} and x_{dI} vs x_w in the column I based on three equilibrium stages and total reflux ratio.

Table A.2. The algebraic equations of the given differential equations derived from finite difference approximation (explicit method)

Differential equation	Algebraic equation
$C_A = f(z, t)$	For I = 0
$\varepsilon \dfrac{\partial C_A}{\partial t} = -\dfrac{F}{S}\dfrac{\partial C_A}{\partial z} - k_c a \cdot (C_A - C_A^*)$	$C_{A_{0,j+1}} = \dfrac{(2\alpha C_{Ain} + (-\alpha - k_c a + \beta)C_{A_{0,j}} - \alpha C_{A_{1,j}} + k_c a C^*_{A_{0,j}})}{\beta}$
	For I = 1 to N − 1
	$C_{A_{i,j+1}} = \dfrac{(0.5\alpha C_{A_{i-1,j}} + (-k_c a + \beta)C_{A_{i,j}} - 0.5\alpha C_{A_{i+1,j}} + k_c a C^*_{A_{i,j}})}{\beta}$
	For I = N
	$C_{A_{N,j+1}} = \dfrac{(\alpha C_{A_{N-1,j}} + (-\alpha - k_c a + \beta)C_{A_{N,j}} + k_c a C^*_{A_{N,j}})}{\beta}$
	$\alpha = \dfrac{F}{S\Delta z} \qquad \beta = \frac{\varepsilon}{\Delta t}$
$X_A = f(z, t)$	
$\dfrac{\partial X_A}{\partial t} = \dfrac{k_c \cdot a}{\rho_b}(C_A - C_A^*)$	$X_{A_{i,j+1}} = \dfrac{k_c a \Delta t (C_{A_{i,j}} - C^*_{A_{i,j}})}{\rho_b}$
$C_A{}^*$ versus X_A	$C^*{}_{A_{i,j}} = HX_{A_{i,j}}$

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