

Composition Estimation of Reactive Batch Distillation by Using Adaptive Neuro-Fuzzy Inference System

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Abstract Composition estimation plays very important role in plant operation and control. Extended Kalman filter (EKF) is one of the most common estimators, which has been used in composition estimation of reactive batch distillation, but its performance is heavily dependent on the thermodynamic modeling of vapor-liquid equilibrium, which is difficult to initialize and tune. In this paper an inferential state estimation scheme based on adaptive neuro-fuzzy inference system (ANFIS), which is a model base estimator, is employed for composition estimation by using temperature measurements in multicomponent reactive batch distillation. The state estimator is supported by data from a complete dynamic model that includes component and energy balance equations accompanied with thermodynamic relations and reaction kinetics. The mathematical model is verified by pilot plant data. The simulation results show that the ANFIS estimator provides reliable and accurate estimation for component concentrations in reactive batch distillation. The estimated states form a basis for improving the performance of reactive batch distillation either through decision making of an operator or through an automatic closed-loop control scheme.

Keywords reactive batch distillation, multicomponent, pilot plant, adaptive neuro-fuzzy inference system, state estimation

1 INTRODUCTION

Reactive batch distillation is a renowned unit operation widely used in industries. Composition monitoring and composition control play an essential role in the plant. Especially, in order to meet the purity specifications, the batch column has to be operated as precisely as possible. Depending on the market conditions and economic incentives, the variety and amount of products should be readily changed. Oisiovisci and Cruz developed a stochastic estimator for batch distillation columns, a discrete extended Kalman filter (EKF) for binary and multicomponent systems, and tested them. Accurate composition estimate and fast convergence were obtained, in which the EKF presents its ability to incorporate the effects of noise (from both measurement and model). The filter performance was usually improved when larger sets of secondary measurements were used, and/or when the sampling frequency was increased. However, these options increased the complexity of estimator and the computational burden [1, 2]. Venkateswarlu and Avantiika used various methods based on extended Kalman filter, adaptive fading Kalman filter and steady state Kalman filter for inferential estimation of compositions from temperature measurements in multicomponent batch distillation. They showed better suitability of the EKF and pointed out the difficulty in tuning its covariance matrices [3]. Olanrewaju and Al-Arfaj exhibited that a state estimator could be successfully designed and implemented in a feedback control system of reactive distillation. They examined the control performance of a system that relies on the state estimator and compared it to a system that takes direct

measurement from the process assuming the availability of a perfect online analyzer. The estimator-based system is robust against moderate measurement errors and erroneous initial conditions. It is shown that if the state estimator is designed from a highly erroneous process model, noisy measurements and approximate initial conditions, the use of estimator together with an online analyzer (for easily measured states) is recommended to achieve an effective control of a reactive distillation system [4]. Venkateswarlu and Kumar presented an inferential state estimation scheme based on EKF with optimal selection of sensor location using principal component analysis (PCA) for composition estimation in multicomponent reactive distillation. They supported this state estimator by a simplified dynamic model of reactive batch distillation that includes component balance equations together with thermodynamic relations and reaction kinetics, and demonstrated that the EKF estimation scheme with optimal temperature sensor configuration is effective for inferential estimation of compositions in multicomponent reactive batch distillation [5]. Zamproga *et al.* exploited the properties of two multivariate regression techniques, principal component analysis and partial least squares (PLS) regression, to develop soft sensors to estimate the product composition profiles in a simulated batch distillation process using available temperature measurements, and demonstrated that the PLS estimators could provide accurate composition estimations for a batch distillation process. The computational requirements are very low, which makes the estimators attractive for on-line use. However, the performance of EKF depends on the thermodynamic modeling of vapor-liquid equilibrium, which is also difficult to initialize and tune, and requires considerable computational effort for

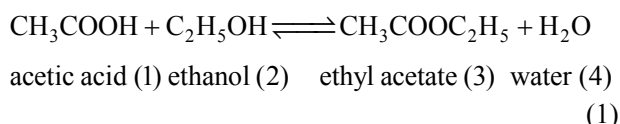
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on-line use [6]. Bahar and Özgen designed an artificial neural network (ANN) estimator to predict the composition values of a reactive batch distillation system inferentially. They used the reflux ratio of the batch distillation column as input to the ANN as well as temperature values. The performance of the network was tested in open-loop and the product compositions could be predicted by employing the ANN estimator, which can be used in the control of product compositions [7]. Fernandez de Canete *et al.* applied an adaptive network based fuzzy inference system (ANFIS) predictor to estimate the product compositions in a binary methanol-water continuous distillation column from available on-line temperature measurements, in which genetic algorithms were used to automatically select the optimum control signal based on an ANFIS model of the plant. Further, they tested the performance of the ANFIS estimator by observing the performance of the dual control system for both set point tracking and disturbance rejection cases [8]. This control strategy is potential in areas of design related to operability and control in process engineering. In the present work ANFIS estimators are designed to infer the distilled compositions from the measurable tray temperatures in a reactive batch distillation column of pilot plant.

2 APPLICATION SYSTEM

In order to design and implement the proposed state estimation scheme, a reactive batch distillation with an esterification reaction is considered. The reversible reaction is given by



The reaction mixture involves four azeotropes, three homogenous azeotropes of ethyl acetate-ethanol, ethanol-water and ethyl acetate-ethanol-water and one heterogenous azeotrope of acetic acid-water. Reactive batch distillation can overcome azeotropes by changing or getting rid of the conditions for azeotrope formation through the combined effect of reaction and separation. Because of the lowest boiling point of ethyl acetate, it is the main product in the mixture. The chemical equilibrium is shifted to the right and the conversion of reactants is improved by controlling the ethyl acetate removal. Specifications of the column are shown in Table 1, in which the kinetic model for this chemical reaction system is given by Venkateswarlu and Kumar [5].

3 SIMULATION METHODOLOGY

In this study, all the data required for training procedure of ANFIS estimator are generated from the dynamic simulation of the reactive batch distillation column. The simulation is performed by solving the

Table 1 Characteristics and operation conditions of the reactive batch distillation for verification

Parameters	Value
No. of plates	20
initial charge/kmol	0.5
initial mole fraction	
CH ₃ COOH (1)	0.35
C ₂ H ₅ OH (2)	0.45
CH ₃ COOC ₂ H ₅ (3)	0
H ₂ O (4)	0.2
condenser pressure/kPa	101.325
condenser volume/m ³	0.005
column diameter/m	0.08
WHS/m	0.013
WLS/m	0.0236
$Q_B/\text{kJ}\cdot\text{h}^{-1}$	3587.2
kinetic data $r = k_1 C_1 C_2 - k_2 C_3 C_4$	
$k_1/\text{kmol}^{-1}\cdot\text{h}^{-1}$	28.56
$k_2/\text{kmol}^{-1}\cdot\text{h}^{-1}$	9.78

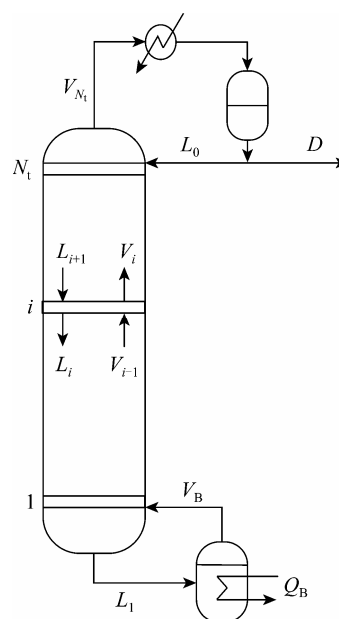


Figure 1 Experimental reactive batch distillation column

differential and algebraic equations (DAE) simultaneously with the numerical integration method. For these purposes, the process is modeled by using a tray-by-tray description, resulting in 88 differential equations. The equations describing the process are given in Appendix A and the thermodynamic model is given in Appendix B. For verification of the mathematical model, an experimental setup (Fig. 1) was considered [9]. Characteristics of the experimental column are shown in Table 1. The column was operated at

total reflux conditions for approximately 4.5 hours, then, in approximately one hour, it yielded distillate products with no reflux.

4 STATE ESTIMATION ALGORITHM

Composition control of batch or continuous reactive distillation processes is very important. Especially, in order to meet the purity specifications, the batch column has to be operated as precisely as possible. If the current compositions are known, they can form a basis to improve the process performance through the decision making of an operator for the development of a closed loop control scheme. However, composition measurement is not feasible, since, the analyzers, such as gas chromatographs, subject to measurement delay as well as high investment and maintenance costs. As an alternative, compositions can be estimated from temperature measurements. Thus, the estimator that utilizes temperature measurements can be used to infer the product compositions. In this study, the ANFIS methodology and a hybrid structure are used to estimate the compositions from tray temperatures.

4.1 Selection of measurement points

Yu *et al.* [10] employed a degree-of-freedom concept to analyze the observability of distillation column and exhibited that, if the number of measurements is at least $(N_C - 1)$, the distillation column will be observable. Other investigators [11, 12] showed the same results for multi-component batch distillation column by using extended Luenberger observer and extended Kalman filter, respectively. They showed that at least (N_C) thermocouples were needed for effective estimation [11, 12]. Increasing the number of temperature measurements above N_C does not result in better performance. The temperature measurement locations should be spread throughout the column uniformly including the reboiler and the top tray [12]. The reboiler and the top tray are the most sensitive locations for temperature measurement in a multi-component batch distillation column [5]. In this study, ANFIS architecture is designed for composition estimation by using the measured tray temperatures. However, since ANFIS has a single output, only one of the product compositions can be estimated using the temperature values. Therefore, four parallel ANFIS estimators are used to estimate the distilled compositions. While the number of measurements is increased with the system inputs, structure complexity is increased, which affects the convergence of the problem. Therefore, it is decided to use three-tray measurement for estimation process. In order to find the best location of the three sensors the following method is used. First, we fix two sensors on top and bottom trays and then search the location of the third sensor by computing the average mean integral square error (AMISE).

4.2 ANFIS-based state estimation

The basic idea behind the neuro-adaptive learning techniques is simple. These techniques provide a method for the fuzzy modeling procedure to learn information about data set, in order to compute the membership function parameters that best allow the associated fuzzy inference system to track the given input-output data. ANFIS constructs an input-output mapping based on both human knowledge (in the form of fuzzy if-then rules) and simulated input-output data pairs. It serves as a basis for building the set of fuzzy if-then rules with appropriate membership functions to generate the input-output pairs. We will describe primarily architecture and this learning algorithm for the Sugeno fuzzy model, with an application example of state estimation for reactive batch distillation.

4.3 ANFIS architecture

In this study, the artificial neural network and fuzzy logic are combined to establish a fuzzy neural network. The linear fuzzy rule in a Takagi and Sugeno's (TS) fuzzy model with 5 inputs has the form of

R^m : If X_1 is A_{1j} , X_2 is A_{2j} , X_3 is A_{3j} , X_4 is A_{4j} , X_5 is A_{5j} ,
Then

$$y^m = \left(\sum_{i=1}^5 r_i^m X_i \right) + r_0^m, \quad i = 1, 2, \dots, 5; \quad (2)$$

$$j = 1, 2, \dots, n; \quad m = n^5$$

where R^m denotes the m th fuzzy rule, X_i the i th input parameter, i the number of input parameters, j the number of membership functions, A_{ij} a fuzzy subset, y^m the output for the m th fuzzy rule, and r_i^m the i th parameters for the conclusion part of the m th fuzzy rule. Fig. 2 depicts the ANFIS structure, which is a five feedforward connective network to realize a simplified TS fuzzy inference system [13–15].

The ANFIS, in essence, integrates the basic elements and functions of a conventional fuzzy inference system (membership functions, fuzzy logic rules, fuzzification, defuzzification, and fuzzy implication) into a connective structure that distributes learning ability to learn the membership functions and fuzzy logic rules. Each input has n membership functions, and nodes of the same layer have similar functions as described below.

● Layer 1: input layer

The input units in this layer are T_1 , T_i , T_{20} , time and reflux ratio, and the output nodes just transmit these input values to the next layer.

$$O_{ij}^{(1)} = X_i, \quad i = 1, 2, \dots, 5; \quad j = 1, 2, \dots, n \quad (3)$$

● Layer 2: linguistic term layer

This layer receives the signals from the input layer and uses the Gaussian 2 membership function to determine the relative contribution of the observed

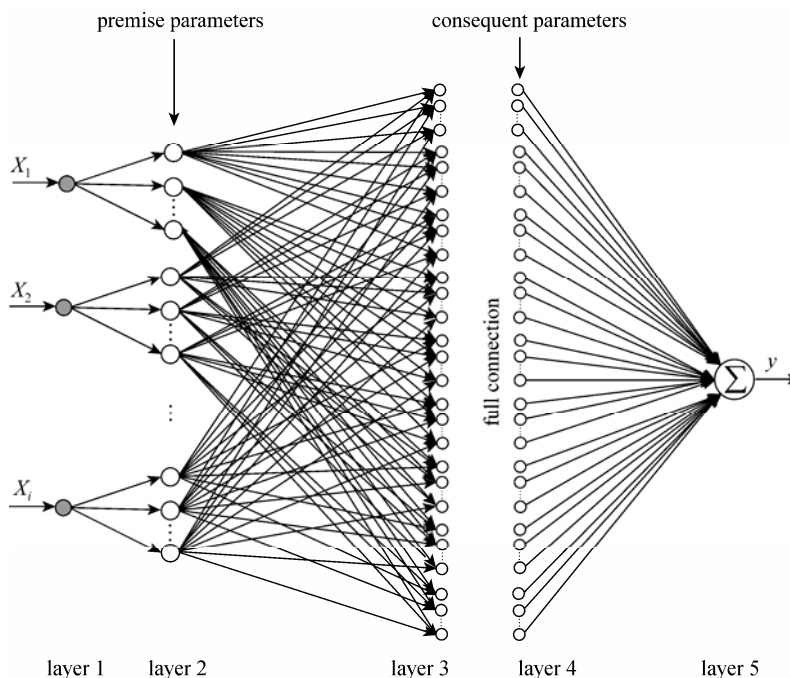


Figure 2 Structure of ANFIS used for state estimation

signals. Thus, the input-output relationship of this layer is defined as follows:

$$O_{ij}^{(2)} = \mu_{A_{ij}} = \exp \left[-\frac{O_{ij}^{(1)} - a_{ij}^k}{(b_{ij}^k)^2} \right], \quad i = 1, 2, \dots, 5; \\ j = 1, 2, \dots, n; \quad k = 1, 2 \quad (4)$$

The Gaussian 2 membership function implements a membership function based on a combination of two Gaussians. The parameters a_{ij}^1 , b_{ij}^1 and a_{ij}^2 , b_{ij}^2 are the mean and variance defining the left-most and the right-most curve, respectively. Parameters in this layer are referred to premise parameters.

● Layer 3: generate the firing strength

Layer 3 implements the links relating preconditions to consequences. Each output node represents the firing strength of a rule. The connection criterion is that each rule node has only one antecedent link from a linguistic variable. Hence we have

$$O_m^{(3)} = w_m = O_{1j}^{(2)} O_{2l}^{(2)} O_{3p}^{(2)} O_{4q}^{(2)} O_{5q}^{(2)}, \quad j = 1, 2, \dots, n; \\ l = 1, 2, \dots, n; \quad p = 1, 2, \dots, n; \quad q = 1, 2, \dots, n; \quad m = n^5 \quad (5)$$

● Layer 4: consequent layer

Each node in this layer is an adaptive node with a node function

$$O_m^{(4)} = O_m^{(3)} f_m = \frac{w_m}{\sum_{m=1}^{n^5} w_m} \left[\left(\sum_{i=1}^5 r_i^m X_i \right) + r_o^m \right], \\ i = 1, 2, \dots, 5; \quad m = n^5 \quad (6)$$

Parameters in this layer are referred to consequent parameters.

● Layer 5: output layer

The single node in this layer is a fixed node labeled Σ , which computes the overall output as the summation of all incoming signals:

$$O^{(5)} = y = \sum_{m=1}^{n^5} O_m^{(4)}, \quad m = n^5 \quad (7)$$

Apparently, the ANFIS presented is equivalent to a simplified fuzzy inference system, where layers 1 and 2 correspond to the antecedent part of the fuzzy rules, and layers 3, 4 and 5 correspond to the conclusion part.

5 RESULTS AND DISCUSSION

The simulation methodology presented in Section 3 is considered to generate different data sets for training the ANFIS estimator. Fig. 3 shows the composition profile of the condenser with respect to time for total reflux. It indicates that compositions reach a steady state condition with total reflux after 900 minutes. The condenser composition for reflux ratio of 4 is plotted in Fig. 4. Since ethyl acetate (EtAc) is the lightest distillate component, and its withdrawal from the column will cause the chemical equilibrium to shift to the right, so its variation shows a maximum in the operation. Fig. 5 shows the variation of EtAc mole fraction in the condenser with respect to time for different reflux ratios.

For verification of the mathematical model, the temperature profiles of different trays are compared with model results, as shown in Figs. 6 and 7. In 250 minutes of the operation the temperatures are reduced because of the total reflux operation and ethyl acetate

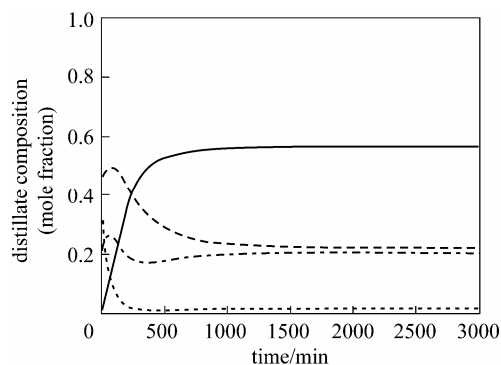


Figure 3 Condenser profile for total reflux
 acetic acid; ---- ethanol; — EtAc; -.- water

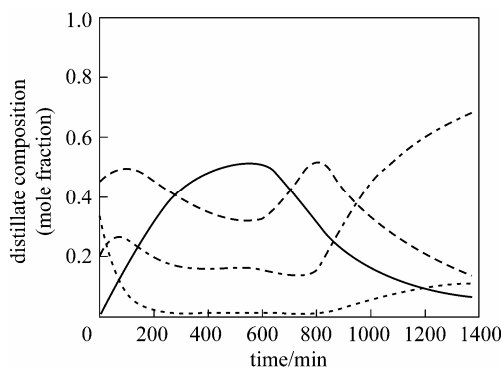


Figure 4 Condenser profile for reflux ratio of 4
 acetic acid; ---- ethanol; — EtAc; -.- water

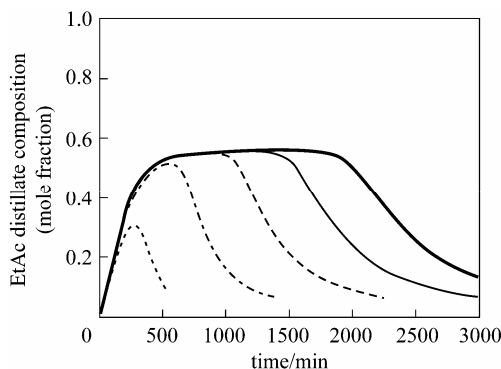


Figure 5 EtAc mole fraction in the condenser for different reflux ratios with $Q_B = 3587.2 \text{ kJ}\cdot\text{h}^{-1}$
 reflux = 1; ---- reflux = 4; -.- reflux = 7;
 — reflux = 10; — reflux = 13

is produced, which is the lightest component. In the remaining 100 minutes the reflux ratio is equal to 0 and all distilled products are left from the column, which causes the heavy components to come up through the column and makes trays warmer.

In this study, ANFIS architecture is utilized to estimate the distilled compositions in a reactive batch distillation column using the measured tray temperatures. Four parallel ANFIS estimators are designed and combined to estimate the top product compositions from tray temperatures. Also, as it is stated in

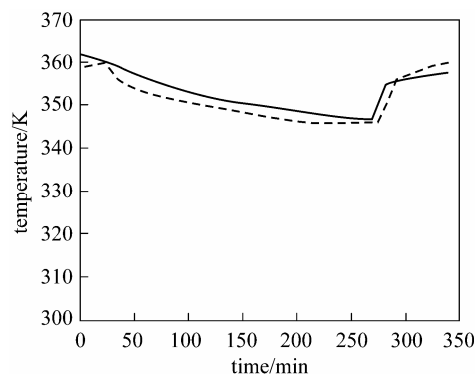


Figure 6 Temperature profile of tray number 3
 — simulation; ---- Exp.

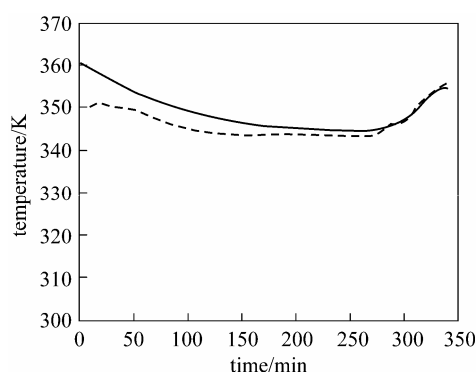


Figure 7 Temperature profile of tray number 18
 — simulation; ---- Exp.

Section 4 temperatures of three trays are utilized for estimation.

After training of the ANFIS structure, the performance of estimators is investigated through the model. The temperature data of every sampling time is corrupted with a zero mean random Gaussian noise with a standard deviation of 0.2°C . The temperature data with this noise is considered as the base case data. The accuracy of the state estimator is assessed by using an average mean integral squared error (AMISE), which is given by

$$\text{AMISE} = \frac{1}{N_R} \sum_{j=1}^{N_R} \sqrt{\frac{\sum_{i=1}^{N_S} (X_{\text{EtAc}} - \hat{X}_{\text{EtAc}})^2}{N_S}} \quad (8)$$

The AMISE calculation is based on the estimated and actual product compositions of ethyl acetate for different reflux ratios. Actual compositions are defined as those obtained from the numerical simulation of the dynamic model of reactive batch distillation. The estimated compositions are those predicted by the estimator. Table 2 shows the AMISE for the various sensor configurations. As mentioned in Section 4.1 the third sensor is selected by searching for minimum AMISE.

Figures 8 (a)–(d) show the comparison of acetic acid, ethanol, ethyl acetate and water compositions, respectively. These results are obtained by introducing -3% step change in reflux ratio. Fig. 9 shows the

Table 2 Average mean integral squared error for sensor configuration

Measurement trays	AMISE	Measurement trays	AMISE
T ₁ , T ₂ , T ₂₀	0.0030	T ₁ , T ₁₁ , T ₂₀	0.0046
T ₁ , T ₃ , T ₂₀	0.0033	T ₁ , T ₁₂ , T ₂₀	0.0096
T ₁ , T ₄ , T ₂₀	0.0030	T ₁ , T ₁₃ , T ₂₀	0.0026
T ₁ , T ₅ , T ₂₀	0.0025	T ₁ , T ₁₄ , T ₂₀	0.0056
T ₁ , T ₆ , T ₂₀ ^①	0.0021	T ₁ , T ₁₅ , T ₂₀	0.0042
T ₁ , T ₇ , T ₂₀	0.0051	T ₁ , T ₁₆ , T ₂₀	0.0026
T ₁ , T ₈ , T ₂₀	0.0032	T ₁ , T ₁₇ , T ₂₀	0.0045
T ₁ , T ₉ , T ₂₀	0.0026	T ₁ , T ₁₈ , T ₂₀	0.0024
T ₁ , T ₁₀ , T ₂₀	0.0042	T ₁ , T ₁₉ , T ₂₀	0.0024

① Optimum configuration.

comparison of estimated ethyl acetate composition by -5% disturbances in heat duty of reboiler through batch time notwithstanding -3% changes in reflux ratio. In spite of the fact, reboiler heat duty was fixed through all training data that ANFIS estimator was

designed with. The actual reflux ratio was 9 and in order to reflect the real situation, the temperature data of every sampling period is corrupted with random Gaussian noise of zero mean with a standard deviation of $0.2\text{ }^{\circ}\text{C}$. In order to show the robustness of ANFIS estimator we increase input noise to $0.4\text{ }^{\circ}\text{C}$. As mentioned above all training data corrupted with $0.2\text{ }^{\circ}\text{C}$ noises and the result is showed in Fig. 10.

6 CONCLUSIONS

Reactive distillation is an attractive process intensification scheme involving combined operations of reaction and separation in a single unit. Since composition estimation is an important issue concerning operation and control of reactive batch distillation process, an inferential state estimation scheme based on ANFIS is employed for composition estimation with temperature measurements. The estimator results show that the ANFIS provides reliable and accurate estimation for component concentrations in reactive batch distillation. The estimated states form a basis to improve the performance of reactive batch distillation either through the decision making of an operator or through an automatic closed-loop control scheme.

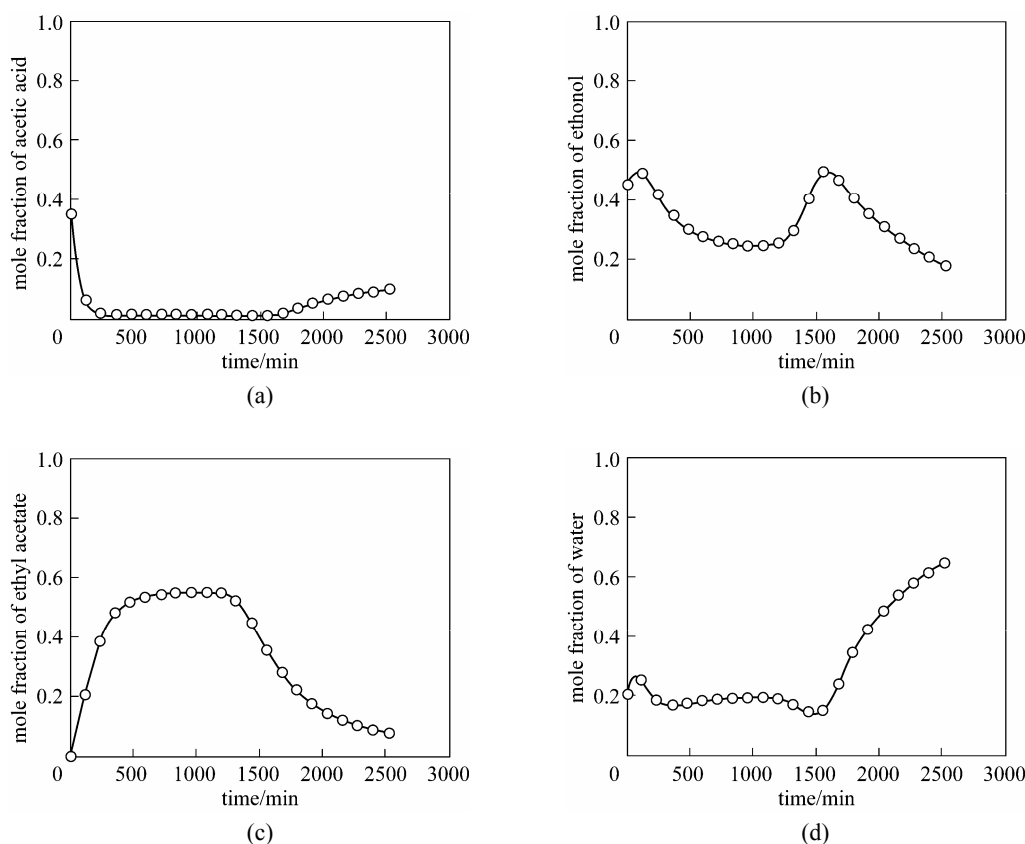


Figure 8 Comparison of ANFIS with simulation results for (a) acetic acid, (b) ethanol, (c) ethyl acetate, and (d) water mole fraction by -3% step change in reflux ratio
— ANFIS; ○ simulation

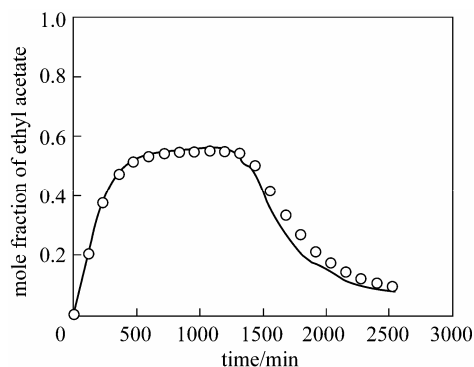


Figure 9 Comparison of ANFIS with simulation result for ethyl acetate composition by -3% step change in reflux ratio and -5% disturbances in reboiler heat duty
— ANFIS; ○ simulation

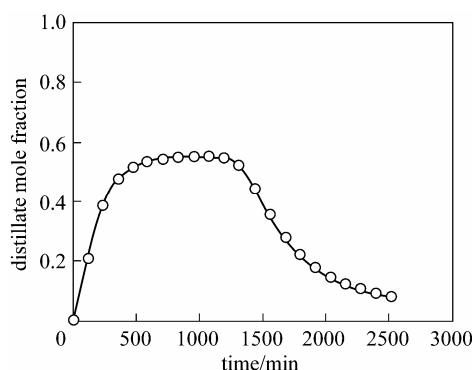


Figure 10 Comparison of ANFIS with simulation results for ethyl acetate composition by -3% step change in reflux ratio and 0.4 °C noises in measuring tray temperature
— ANFIS; ○ simulation

NOMENCLATURE

AMISE	average mean integral squared error
D	distillate flow rate, $\text{kmol}\cdot\text{h}^{-1}$
L	liquid flow rate, $\text{kmol}\cdot\text{h}^{-1}$
M	molar liquid holdup on tray, kmol
Q_R	reboiler heat input, $\text{kJ}\cdot\text{h}^{-1}$
R	reaction rate, $\text{kmol}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$
V	vapor flow rate, $\text{kmol}\cdot\text{h}^{-1}$
WHS	weir height, m
WLS	weir length, m

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APPENDIX A Mathematical model of reactive batch distillation process

For the reboiler, the total and species mass balance and energy balance are as follows (subscript B):

$$\frac{dM_B}{dt} = L_1 - V_B + M_B \Delta R_B, \quad (\text{A1})$$

$$\frac{d(M_B x_{B,j})}{dt} = L_1 x_{1,j} - V_B y_{B,j} + M_B R_{B,j}, \quad j = 1, \dots, N_C, \text{ and} \quad (\text{A2})$$

$$\frac{d(M_B H_{L,B})}{dt} = L_1 H_{L,1} - V_B H_{V,B} + Q_B. \quad (\text{A3})$$

First plate (subscript 1):

$$\frac{dM_1}{dt} = V_B + L_2 - V_1 - L_1 + M_1 \Delta R_1, \quad (\text{A4})$$

$$\frac{d(M_1 x_{1,j})}{dt} = V_B y_{B,j} + L_2 x_{2,j} - V_1 y_{1,j} - L_1 x_{1,j} + M_1 R_{1,j}, \quad j = 1, \dots, N_C, \text{ and} \quad (\text{A5})$$

$$\frac{d(M_1 H_{L,1})}{dt} = V_B H_{V,B} - V_1 H_{V,1} + L_2 H_{L,2} - L_1 H_{L,1}. \quad (\text{A6})$$

Intermediate plates (subscript i):

Table B1 NRTL model parameters

Comp.i	Comp.j	a_{ij}	a_{ji}	b_{ij}	b_{ji}	α_{ij}
acetic acid(1)	ethanol(2)	0	0	-252.482	225.4756	0.3
acetic acid (1)	ethyl acetate(3)	0	0	-235.279	515.8212	0.3
acetic acid (1)	H ₂ O(4)	-1.9766	3.3293	609.8886	723.888	0.3
ethanol(2)	ethyl acetate(3)	1.817306	-4.41293	-421.289	1614.287	0.1
ethanol(2)	H ₂ O(4)	0.806535	0.514285	-266.533	444.8857	0.4
ethyl acetate(3)	H ₂ O(4)	-2.34561	3.853826	1290.464	-4.42868	0.364313

$$\frac{dM_i}{dt} = V_{i-1} + L_{i+1} - V_i - L_i + M_i \Delta R_i, \quad (A7)$$

$$\frac{d(M_i x_{i,j})}{dt} = V_{i-1} y_{i-1,j} - V_i y_{i,j} + L_{i+1} x_{i+1,j} - L_i x_{i,j} + M_i R_{i,j},$$

$$j = 1, \dots, N_C, \text{ and} \quad (A8)$$

$$\frac{d(M_i H_{L,i})}{dt} = V_{i-1} H_{V,i-1} - V_i H_{V,i} + L_{i+1} H_{L,i+1} - L_i H_{L,i} \quad (A9)$$

Top plate (subscript N_i):

$$\frac{dM_{N_i}}{dt} = V_{N_i-1} + L_0 - V_{N_i} - L_{N_i} + M_i \Delta R_{ii}, \quad (A10)$$

$$\frac{d(M_{N_i} x_{N_i,j})}{dt} = V_{N_i-1} y_{N_i-1,j} + L_0 x_{D,j} - L_{N_i} x_{N_i,j} -$$

$$V_{N_i} y_{N_i,j} + M_{N_i} R_{N_i,j},$$

$$j = 1, \dots, N_C, \quad (A11)$$

and

$$\frac{d(M_{N_i} H_{L,N_i})}{dt} = V_{N_i-1} H_{V,N_i-1} - V_{N_i} H_{V,N_i} + L_0 H_{L,D} - L_{N_i} H_{L,N_i}. \quad (A12)$$

Condenser (subscript D):

$$\frac{dM_D}{dt} = V_{N_i} - L_0 - D + M_D \Delta R_D, \text{ and} \quad (A13)$$

$$\frac{d(M_D x_{D,j})}{dt} = V_{N_i} y_{N_i,j} - D x_{D,j} - L_0 x_{D,j} + M_D R_{D,j},$$

$$j = 1, \dots, N_C. \quad (A14)$$

The holdups of the trays are calculated based on Luyben (1990)

$$LV = L \times Mw_{Ave} / \text{Density}_{Ave},$$

$$\text{HFW} = \left(\frac{LV}{999 \times \text{WLS}} \right)^{0.6667}, \quad (A15)$$

$$MV = \left(\text{HFW} + \frac{\text{WHS}}{12} \right) \times \frac{\pi d^2}{4 \times 144}, \text{ and}$$

$$M = MV \times \text{Density}_{Ave} / Mw_{Ave}.$$

The reboiler holdup at any time is calculated from an algebraic combination of the initial charge, the material in the column, and the total material removed up at that instant [16]:

$$M_B = M_{B0} + \sum_{i=1}^{N_i} M_{i0} - \sum_{i=1}^{N_i} M_i - \int D dt \quad (A16)$$

APPENDIX B The thermodynamic model

The thermodynamic model used in this study is a nonrandom two-liquid (NRTL) model based on Lee *et al* [17]:

$$\ln \gamma_i = \frac{\sum_{j=1}^{N_C} \tau_{ji} G_{ji} X_j}{\sum_{k=1}^{N_C} G_{ki} X_k} + \sum_{j=1}^{N_C} \frac{G_{ji} X_j}{\sum_{k=1}^{N_C} G_{kj} X_k} \left[\tau_{ij} - \frac{\sum_{k=1}^{N_C} X_k \tau_{ki} G_{kj}}{\sum_{k=1}^{N_C} G_{kj} X_k} \right], \quad (B1)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad \tau_{ij} = a_{ij} + b_{ij} / T, \quad \alpha_{ij} = \alpha_{ji}, \quad \tau_{ii} = \tau_{jj} = 0.$$

The parameters of NRTL model are used to predict the composition and temperature. The complete set of NRTL parameters is given in Table B1.