

## Dynamic Simulation of Semi-Batch Catalytic Distillation Used for Esterification Reaction

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### Abstract

In this paper the detailed mathematical dynamic model of semi-batch reactive distillation is formulated for ethyl acetate synthesis (esterification reaction).

The model is composed of material balance, heat balance, and equilibrium equations. The set of nonlinear ordinary differential equations governing the unsteady state composition profile in a semi-batch reactive distillation column were solved by using fourth order Runge-Kutta integration method with the aid of the powerful MATLAB 6.5 program which used to simulate and optimize the semi-batch reactive distillation column.

The simulation provides compositions, temperatures and holdups profiles along the column as a function of time. Also the reactant conversion and ethyl acetate purity in distillate are calculated.

Finally, the simulation results are analyzed to find the optimum operating policy of reflux ratio, Ethanol/Acetic acid and catalyst weight.

**Keywords:** Reactive distillation, esterification, semi-batch operation, dynamic simulation.

الخلاصة

(Reactive Distillation)

(Semi-batch)

(Unsteady state)

MATLAB 6.5

Fourth Order Runge-Kutta

(Reboiler, Column and condenser )

(Ethyl Acetate)

(Reflux Ratio) (Catalyst Weight) and , (Ethanol/Acetic acid ratio)

### 1. Introduction

Reactive distillation is an operation in which separation and chemical reaction take place simultaneously within a fractional distillation column. It can be used for a liquid phase reactions systems in three cases: when the reaction needs large excess of one or more reactants, when an equilibrium state can be moved by removal of one or more products as their concentration is increased, or when the product separation is difficult due to azeotrope formation. Reactive distillation offers several important advantages such as reduction in total costs and energy consumption, overcoming of thermodynamic limitations, (e.g. azeotropes) and increased reaction yield and selectivity [1, 2].

Generally, the design and control of reactive distillation is more difficult because of the complicated interactions between vapour-liquid equilibrium, reaction kinetics and hydraulics of the column. Therefore, such interaction processes lead to complicated dynamic behaviour of the system.

Cuille and Reklaitis [3] considered the simulation of reactive batch distillation with reaction occurring on the plates, in the condenser and in the reboiler. The model was posed as a system of differential and algebraic equations (DAEs) and a stiff

solution method was employed for integration. Wilson [4] considered design and operation of batch reactive distillation. Mujtaba and Macchietto [5] proposed polynomial curve fitting techniques to optimize reactive batch distillation of ethyl acetate. In their work they neglected the energy balance and changes in molar hold-ups. Francis et al. [6] used reduced model to study the trade off between model accuracy and computational tractability for model-based control applied for batch reactive distillation column used for esterification reaction. Then, they used the reduced model in a model predictive control algorithm.

Monroy and Alvarez [7] have developed a nonlinear PID-type top product composition controller for ethyl acetate process operated in batch mode, using reflux ratio as the manipulated variable. They showed that their scheme generates the same reflux ratio profile as the optimization-based approach followed by Mujtaba and Macchietto [5]. Ismail et al. [8] studied experimentally the ethyl acetate production in a packed bed reactive distillation column operated in batch and continuous modes. The effects of the variables such as the reflux ratio, vapor rate and feed flow rate on ethyl acetate production. They found that, the packed bed reactive distillation

column operated in continuous mode gave the highest ethyl acetate composition. Vora and Daoutidis [9] studied the dynamics and control of an ethyl acetate reactive distillation system and proposed a new feed configuration for the two reactants that allows higher conversion and purity than the conventional configuration, which involves feeding in a single tray.

On the other hand, Mujtaba et al. [10] replaced rigorous dynamic model of batch reactive distillation by a neural network based model which can predict the column dynamics very well in few CPU seconds. A simple esterification reaction system is used in the batch reactive distillation column to demonstrate the ideas. Lee et al. [11] studied a batch reactive distillation with double-feed, they concluded that, this types of columns cannot produce pure ethyl acetate for the stoichiometric feeding of acetic acid and ethanol. They state that a higher reflux ratio is more harmful to the overall reaction conversion. Espinosa [12] developed a dynamic conceptual model for batch reactive distillations. He assumed a rectifier with an infinite number of stages. He concluded that, the operation at constant reflux is very easy to implement in practice. Patel et al. [13] derived a mathematical model and simulation of reactive batch distillation column for ethyl acetate synthesis. The DAEs which

represent the model are solved using fourth order Runge-Kutta method in MATLAB program to obtain the detailed column dynamics.

According to previous literature survey, there are no comprehensive simulations that describe the different process interactions that occur in semi-batch reactive distillation. Therefore, the present study aims to formulate a comprehensive mathematical dynamic model for semi-batch reactive distillation, since such model depends on the analysis of material balance, heat balance, equilibrium, and sum of mole fractions equations.

## **2. Mathematical Model**

The mathematical model of any process is a system of equations whose solution gives a specified data representative of the response of the process to a corresponding set of inputs. The simulation operations make it possible to evaluate the influence of the variables on any process theoretically. The simulation is also used to fix the experimental conditions needed for design, optimization and control.

The boiling point range between acetic acid and ethanol is more than (30 °C), therefore using batch reactive distillation is not useful for this type of systems because the concentration of acetic acid will be much lower than ethanol in reacting zone [14, 15]. For this reason the semi-batch

reactive distillation works by injection of the heavier reacting component above reacting section and the lighter reacting component below reacting section. In the present work a new technique is used by feeding only the heavier component above the reaction section. The semi-batch reactive distillation column is used in this search to increase the reactant conversion because the batch reactive distillation gives lower reactant conversion than semi-batch reactive distillation for the several reasons listed above.

## 2.1 Model Assumptions

The packed reactive distillation column is vertically divided into a number of segments [16]. The condenser and reboiler stages are numbered 1 and N, respectively. The following assumptions were made to simplify the model of semi-batch reactive distillation column [16, 17, 18]:-

1. Neglect of vapor holdup and assume total condensation.
2. Perfect mixing on all stages and in all vessels (condenser and reboiler), and the condenser and the reboiler are treated as equilibrium stages.
3. Ideal vapor phase for all components in mixture.
4. Liquid and vapor phases in thermodynamic phase equilibrium.

## 2.2 Estimation of Model Parameters

### a. Equilibrium Relations

### Dynamic Simulation of Semi-Batch Catalytic Distillation

Used for Esterification Reaction

For non-ideal mixture additional variable  $\gamma_i$  appears to represent the degree of deviation from ideality.

$$K_i = \frac{\gamma_i \cdot P_i}{P} \quad \dots (1)$$

Many models were presented to predict the liquid phase activity coefficient ( $\gamma_i$ ) such as Wilson, NRTL, UNIFAC and UNIQUAC. Of all of these models the NRTL model was used because this model gives fewer error than other models. Table (2) contains parameters of NRTL model for all components used in this study.

### b. Antoine Model

The Antoine equation is used to calculate the vapor pressure of each component

$$\ln(P^\circ) = C_1 + \frac{C_2}{T} + C_3 \log(T) + C_4 T^{C_5} \quad \dots (2)$$

where the temperature T is in Kelvin and the pressure in kPa.

Table (3) contains parameters of Antoine equation for all components [19].

### c. Bubble Point Calculation

The temperature on each tray was evaluated by trial and error method to calculate the bubble point. The bubble point is calculated by Newton's method, thus according to this method in each trial the improved

temperature was calculated by applying Newton's formula;

$$T_{n+1} = T_n - \frac{f(T)}{f'(T)} \quad \dots (3)$$

where

$$f(T) = \sum_{i=1}^c K_i x_i - 1 \quad \dots (4)$$

$$f'(T) = \sum_{i=1}^c x_i \frac{dK_i}{dT} \quad \dots (5)$$

It was found that (0.0001 °C) accuracy could be reached by making five trials.

**d. Enthalpy Calculation**

The enthalpy of vapor and liquid phases is calculated by using the following equations.

$$H_{j,i} = \int_{T_r}^{T_2} C_{p_i}^V dT \quad \dots (6)$$

$$h_{j,i} = \int_{T_r}^{T_2} C_{p_i}^L dT \quad \dots (7)$$

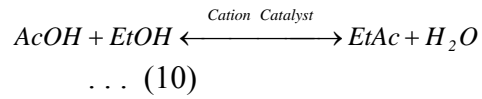
$$H_j = \sum_{i=1}^c H_{j,i} y_{j,i} \quad \dots (8)$$

$$h_j = \sum_{i=1}^c h_{j,i} \cdot x_{j,i} \quad \dots (9)$$

For each component, the vapor or liquid specific heat is related to a temperature by using a polynomial. Table (4) contains a polynomial which can be used to evaluate the vapor and liquid specific heat (C<sub>p</sub>) as a function of temperature.

**e. Reaction rate**

In the present study, the esterification of ethanol (EtOH) and acetic acid (AcOH), to produce ethyl acetate (EtAc) is studied as shown in the following reaction:



This reaction is reversible, and the equilibrium composition is a weak function of temperature. The forward reaction rate (ester formation, R<sub>1</sub>) is a function of EtOH and AcOH concentrations, and the reverse reaction rate (ester hydrolysis, R<sub>2</sub>) is a function of EtAc and water. The selected catalyst type that used in present model is the ion exchange resin named (Purolite CT179) [14], the kinetic equations are given below:

$$R_1 = k_1 x_{EtOH} x_{AcOH}^{1.5} \quad \dots (11)$$

$$R_2 = k_2 x_{EtAc} x_{H_2O} \quad \dots (12)$$

The equilibrium constant K<sub>eq</sub> is given by the equation:

$$K_{eq} = \frac{k_2}{k_1} = \frac{x_{EtAc} x_{H_2O}}{x_{EtOH} x_{AcOH}^m} \quad \dots (13)$$

All concentrations are given as mole fractions. Both k<sub>1</sub> and k<sub>2</sub> are functions of temperature, according to the Arrhenius equation:

$$k_i = k_{i,0} e^{-E_A / RT} \quad \dots (14)$$

The parameters of Arrhenius equation for the above reaction are shown in Table (5).

**2.3 Model Equations**

Figure (1) represents the semi-batch packed reactive distillation column. In this column, there is vapor liquid equilibrium in the reboiler and condenser, therefore each of reboiler and condenser can be assumed as a theoretical stage. Each stage is assumed to be in thermodynamic equilibrium in

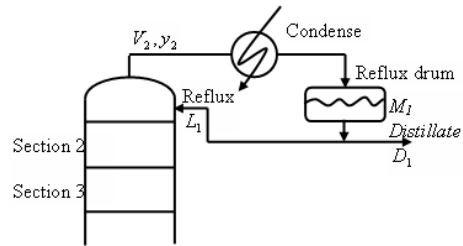
which liquid phase is assumed to be a non-ideal solution and vapor phase an ideal gas mixture. The packing section is divided to ten stages, each stage (15 cm) long. Hence by starting from the upper point of column, the condenser is numbered as stage one and the first section of packing column is numbered stage 2, and so on. The last stage of the packing column is numbered 11, also the reboiler is named stage 12. The model is done to simulate a pilot plant semi-batch reactive distillation column that was constructed in Chemical Engineering Department of University of Technology (Baghdad) [15]. The column specification is given in Table (6).

**Fig.(1) Reactive semi-batch distillation column.**

The acetic acid was fed at a point above reaction section, while the EtOH was added before starting to the reboiler.

The total material, component and energy balances are made to the various sections of the semi-batch reactive distillation column, and by further simplifications of the differential equations lead to the model.

**2.3.1 Condenser**



**a. Total Material Balance on Condenser**

$$\frac{dM_1}{dt} = V_2 - (L_1 + D) \dots (15)$$

**b. Component Material Balance**

$$\frac{d(M_1 x_{i,1})}{dt} = V_2 y_{2,i} - (L_1 + D) x_{i,1} \dots (16)$$

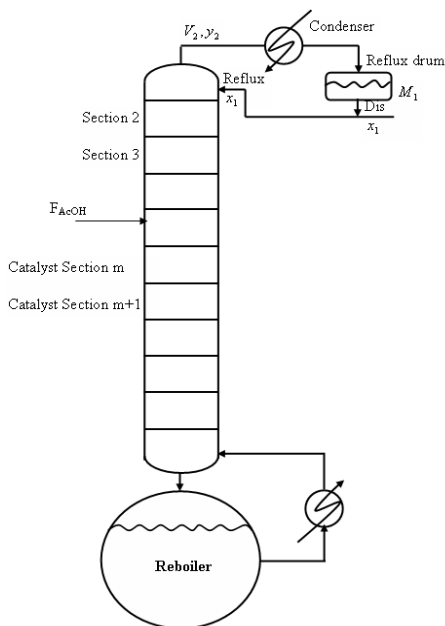
**c. Total energy balance:**

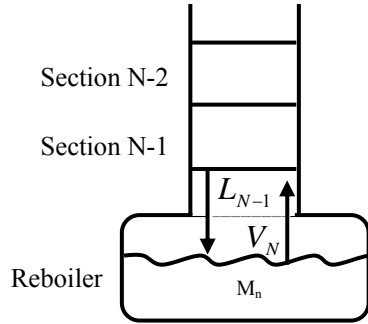
$$\frac{d(M_1 h_1)}{dt} = V_2 H_2 - (L_1 + D) h_1 - Q_c \dots (17)$$

**d. Summation:**

$$\sum_{i=1}^c x_{i,1} - 1 = 0 \dots (18)$$

**2.3.2 Reboiler**





a. Total Material Balance.

$$\frac{dM_N}{dt} = L_{N-1} - V_N \quad \dots (19)$$

b. Component Material Balance

$$\frac{d(M_N \cdot x_{N,i})}{dt} = L_{N-1} x_{N-1,i} - V_N y_{N,i}$$

20)

Expanding the first term of equation (20) and arranging gives.

$$\frac{dx_{N,i}}{dt} = \frac{(V_N - L_{N-1})}{M_N} \cdot x_{N,i} + \frac{L_{N-1}}{M_N} \cdot x_{N-1,i} - \frac{V_N}{M_N} \cdot y_{N,i}$$

... (21)

c. Heat Balance

$$\frac{d(M_N h_N)}{dt} = L_{N-1} h_{N-1} - V_N H_N + Q_R$$

... (22)

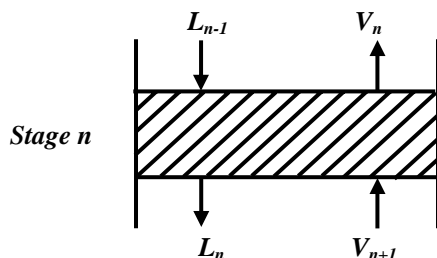
Dividing equation (22) by  $M_N$  and rearranging gives,

$$\frac{dh_N}{dt} = \frac{(V_N - L_{N-1})}{M_N} h_N + \frac{L_{N-1}}{M_N} h_{N-1} - \frac{V_N}{M_N} H_N + \frac{Q}{M_N} \quad \dots (23)$$

d. Summation:

$$\sum_{i=1}^c x_{N,i} - 1 = 0 \quad \dots (24)$$

### 2.3.3 General Stage n



a. Total Material Balance

$$\frac{dM_n}{dt} = L_{n-1} + V_{n+1} - L_n - V_n \quad \dots (25)$$

b. Component Material Balance

$$\frac{d(M_n x_{n,i})}{dt} = L_{n-1} x_{n-1,i} + V_{n+1} y_{n+1,i} - L_n x_{n,i} - V_n y_{n,i}$$

$$\frac{dx_{n,i}}{dt} = \frac{(V_n - L_{n-1} - V_{n+1})}{M_n} x_{n,i} + \frac{L_{n-1}}{M_n} x_{n-1,i}$$

$$+ \frac{V_{n+1}}{M_n} y_{n+1,i} - \frac{V_n}{M_n} y_{n,i}$$

... (27)

c. Energy Balance

$$\frac{d(M_n h_n)}{dt} = L_{n-1} h_{n-1} + V_{n+1} H_{n+1} - L_n h_n - V_n H_n$$

(28)

By substitution eqn. (25) in eqn. (28) then.

$$\frac{dh_n}{dt} = \frac{(V_n - L_{n-1} - V_{n+1})}{M_n} h_n + \frac{L_{n-1}}{M_n} h_{n-1}$$

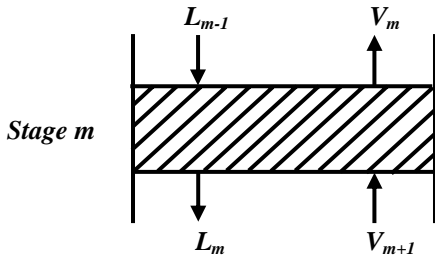
$$+ \frac{V_{n+1}}{M_n} H_{n+1} - \frac{V_n}{M_n} H_n$$

(29)

d. Summation:

$$\sum_{i=1}^c x_{n,i} - 1 = 0 \quad \dots (30)$$

2.3.4 General Reaction stage m



a. Total Material Balance

$$\frac{dM_m}{dt} = L_{m-1} + V_{m+1} - L_m - V_m \dots (31)$$

b. Component Material Balance

$$\frac{d(M_m x_{m,i})}{dt} = L_{m-1} x_{m-1,i} + V_{m+1} y_{m+1,i} - L_m x_{m,i} - V_m y_{m,i} + \epsilon_i W_m R_{m,i} \dots (32)$$

$$\frac{dx_{m,i}}{dt} = \frac{(V_m - L_{m-1} - V_{m+1})}{M_m} x_{m,i} + \frac{L_{m-1}}{M_m} x_{m-1,i} + \frac{V_{m+1}}{M_m} y_{m+1,i} - \frac{V_m}{M_m} y_{m,i} + \frac{\epsilon_i W_m R_{m,i}}{M_m} \dots (33)$$

c. Energy Balance

$$\frac{d(M_m h_m)}{dt} = L_{m-1} h_{m-1} + V_{m+1} H_{m+1} - L_m h_m - V_m H_m + W_m R_{m,i} \Delta H_R \dots (34)$$

By substitution eqn. (31) in eqn. (34) then.

$$\frac{dh_m}{dt} = \frac{(V_m - L_{m-1} - V_{m+1})}{M_m} h_m + \frac{L_{m-1}}{M_m} h_{m-1} + \frac{V_{m+1}}{M_m} H_{m+1} - \frac{V_m}{M_m} H_m + \frac{W_m R_{m,i} \Delta H_R}{M_m} \dots (35)$$

d. Summation:

$$\sum_{i=1}^c x_{m,i} - 1 = 0 \dots (36)$$

The acetic acid feed stage can be treated in the same way of treating stage n but with adding the other term which is the feed term.

With the aid of the finite-difference representation, it is useful to evaluate the values of liquid and vapor enthalpy derivatives  $\frac{dh}{dt}$  and  $\frac{dH}{dt}$  depending on the values of  $h$  and  $H$  at previous time steps, by using the following two equations.

$$\frac{dh}{dt} \approx \frac{h(t) - h(t + \Delta t)}{\Delta t} \dots (37)$$

$$\frac{dH}{dt} \approx \frac{H(t) - H(t + \Delta t)}{\Delta t} \dots (38)$$

These two equations give very good results because the contribution to the energy balance from the change in enthalpy with time is very small.

Also the previous values of molar holdup  $M$  could be used to evaluate the value of the total mass derivative  $\frac{dM}{dt}$  according to the following equation.

$$\frac{dM}{dt} \approx \frac{M(t) - M(t + \Delta t)}{\Delta t} \dots (39)$$

2.4 Dynamic Simulation

This section contains the dynamic simulation of the semi-batch reactive distillation. An MATLAB program was developed to solve the MESH (mass balance, equilibrium relationships, summation and heat balance) equations using fourth order Runge-Kutta technique. The



simulation was carried out by solving the system of differential and algebraic equations simultaneously. In all the simulations presented in this section the initial compositions along the column and in the still are equal to 100% ethanol. Different reflux ratio, ethanol to acetic acid and catalyst weight was used in column simulations. The above model gives a system of ordinary differential equations (ODE'S) and algebraic equations, the algebraic equation includes physical properties and vapor liquid equilibrium equations, where the differential equations include total material, heat and component balance equations. Numerical methods such as finite differences are used to simplify these equations, but they lead to a large number of ordinary differential equations.

Figure (2) shows the flowchart for the computer simulation for semi-batch reactive distillation. Optimum operating policies reflux ratio, Ethanol/Acetic acid and catalyst weight were estimated by simulating the reactive batch distillation column for different but constant reflux ratios thereby maximizing the production rate of ethyl acetate and ethyl acetate purity.

### 3. Model Results

Much more results can be predicted from the dynamic simulation model of semi-batch reactive distillation. The proposed

model can be used to determine the following results:

- Ethyl acetate purity in the accumulated distillate.
- Percent reactant conversion.
- Amount of distillate.
- Stage by stage composition profile.
- Stage by stage temperature profile.
- Stage by stage flow profile.
- Stage by stage molar holdup.

## 4. Results And Discussion

The simulation results are summarized in Table (7), which shows the effect of change in reflux ratio, Ethanol/Acetic acid and catalyst weight, on the accumulated ethyl acetate in distillate, concentration of ethyl acetate in distillate, total batch time. This table shows that the amount of EtAc and EtAc purity obtained in the accumulated distillate increases with increase in reflux ratio but at the expense of higher batch.

### 4.1 Composition and Temperature Profiles

From all 14 simulation runs summarized in Table (7), the results of run 3 are selected to be plotted in Figures (3, 4, 5, 6, 7, 8 and 9). Figures (3, 4, 5 and 6) represent the model results for

ethanol, acetic acid, ethyl acetate and water composition profiles in several locations along the column.

The distillate composition is illustrated in Figure (7). This figure shows that the mole fraction of ethanol in condenser decreases from 1, reaches a steady state value after startup time (0.5 hr after starting) and then gradually falls to zero after 3 hrs. Ethanol mole fraction falls rapidly as it is being consumed by the reaction as well as separated by distillation. The rise in EtAc mole fraction is due to the high rate of reaction initially, however after 2.5 hrs the rate of EtAc production by reaction becomes less than the rate of separation by distillation and therefore there is a fall in the mole fraction of EtAc. Acetic acid concentration gradually increases with time, this behavior is due to acetic acid highest boiling point in the reaction mixture. Acetic acid and ethyl acetate were separated above the acetic acid feed point in the rectification section. Thus, concentrated ethyl acetate and unreacted ethanol will be the first distillation cut and the acetic acid will be the last distillation cut.

The reboiler compositions is plotted in Figure (8). This figure shows that the mole fraction of EtAc in reboiler rises from zero, reaches a small value and then after 2.5 hrs falls to zero. The rise in mole fraction is due to the high rate of reaction initially, however after 2.5 hrs the rate of EtAc

production by reaction becomes less than the rate of separation by distillation and therefore there is a fall in the mole fraction of EtAc. Acetic acid concentration gradually increases with time, this behavior is due to acetic acid highest boiling point in the reaction mixture also that the acetic acid feed was continuous in first 2 hrs, therefore the acetic acid retains in the lower sections of the column. Ethanol mole fraction falls rapidly as it is being consumed by the reaction as well as separated by distillation. Ethanol is completely consumed in 3 hrs, then the reaction stops and the column behaves like a non-reactive batch distillation column.

Figure (9) shows the variation in column temperatures with respect to time. This figure indicates that the reboiler temperature decreases at first and then increases slowly as the reaction proceeds. The initial decrease in temperature is due to more volatile components produced by the reaction, however, as the separation of these components continues, then the reboiler temperature starts increasing.

The model results was compared with the experimental work taken by Ismail et al. [8], and it was found that there is a good agreement in behavior between the mathematical and experimental results.

## 4.2 Optimization Results.

In runs 1 to 5 the reflux ratio was varied from 0.5 to 4. The reflux ratio had a very significant effect on the performance of the semi-batch reactive distillation column. The conversion of the reactants and distillate concentration for five different reflux ratios is shown in Figure (10), indicating that the reactant conversion first rises with increasing reflux ratio and then decreases with further increasing of reflux ratio, this behavior is because EtAc concentration depends on both reaction and separation at the same time. On the other hand, the purity of EtAc in distillate increases with increasing the reflux ratio. The optimum reflux ratio at which the production rate is maximum comes out to be 2. The optimum reflux ratio should be carefully selected to give maximum production rate with appropriate purity.

In runs 3, 6, 7, 8, 9 and 10, the effect of the ratio of acetic acid fed in column to the ethanol on reactant conversion and distillate purity is studied. Figure (11) shows that the reactant conversion relatively increases with increasing the ratio of acetic acid fed in column to the ethanol. Also the distillate purity of ethyl acetate increases but rapidly with increasing the ratio of acetic acid feed in column to the ethanol.

In runs 3, 11, 12, 13 and 14, the effect of catalyst weight on reactant conversion and distillate purity is studied. Figure

(12) shows that conversion and distillate purity of ethyl acetate increase with rapidly with increasing the catalyst weight used in the column. The increase in the reactant conversion with catalyst loading agrees well with the description of literature [10, 14].

### 5. Conclusions

This paper outlines detailed mathematical modeling and simulation of reactive semi-batch reactive distillation column for ethyl acetate production. MATLAB 6.5 program is used to perform the dynamic simulation which is then used to derive the optimum operating profiles.

Column behavior was fully investigated and explained in detail by considering the effects of varying reflux ratio, Acetic acid/Ethanol and catalyst weight.

The optimum operating reflux ratio to give maximum ethyl acetate conversion was found to be 2, while ethyl acetate purity increases with increasing the reflux ratio. The reactant conversion and distillate purity increase with increasing the ratio of acetic acid feed to the ethanol. Also the reactant conversion and distillate purity increase linearly to some limit with increasing amount of catalyst used in column.

The semi-batch reactive distillation gives reactant conversion and product purity higher than batch reactive distillation when the difference in

boiling points of reactants is higher

than 10 °C.

### References

1. Katariya, A. M., Moudgalya, K. M., and Mahajani, S. M., Nonlinear dynamic effects in reactive distillation for synthesis of TAME. *Industrial and Engineering Chemistry Research*, 45(12), 4233–4242 (2006).
2. Reepmeyer, F., Repke, J., & Wozny, G.. Time optimal start-up strategies for reactive distillation columns. *Chemical Engineering Science*, 59, 4339–4347 (2004).
3. Cuille P. E. and Reklaitis G. V. “Dynamic simulation of multicomponent batch rectification with chemical reactions” *Computers & Chemical Engineering*, 10 (4), 389-398 (1986).
4. Wilson, J., *I Chem. Eng. Symp. Ser.*, 100, p 163 (1987).
5. Mujtaba I. M. and Macchietto S. “Efficient optimization of batch distillation with chemical reaction using polynomial curve fitting techniques” *Industrial & Engineering Chemistry Research*, 36 (6), 2287-2295 (1997).
6. Francis J. D. and Lalitha S. B. “Nonlinear Model-Based Control Of A Batch Reactive Distillation Column” *Department of Chemical Engineering University of Delaware, Newark DE*, (1999).
7. Monroy-Loperena R. and Alvarez-Ramirez J. “Output-feedback control of reactive batch distillation columns” *Industrial & Engineering Chemistry Research*, 39, 378-386 (2000).
8. Ismail S. K. , Baris Z. B. and Dramur U.” Esterification of Acetic Acid with Ethanol Catalysed by an Acidic Ion-Exchange Resin” *Turk J Eng.*

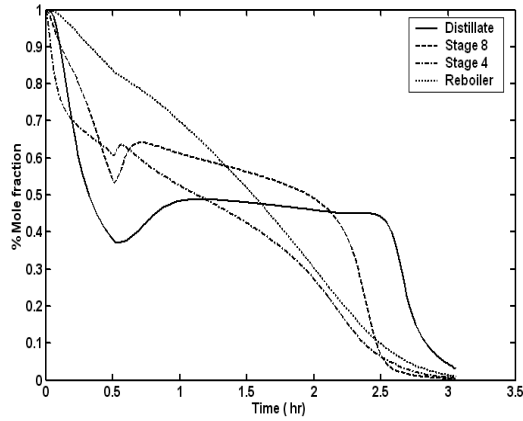
- in Environ Sci, 25, 569-577 (2001).
9. Vora, N., & Daoutidis, P. "Dynamics and control of an ethyl acetate reactive distillation column" Industrial and Engineering Chemistry Research, 40, 833-849 (2001).
  10. Mujtaba M. and Greaves M. A. "Neural Network Based Modeling and Optimization in Batch Reactive Distillation" IChemE (2006)
  11. Lee, J.W., Brüggemann S. and Westerberg A.W. "Visualization of the Ethyl Acetate Reactive Distillation System" Conference proceedings (cdrom). Technical Report LPT-2001-12., March (2001).
  12. Espinosa j. "Assessing the Performance of Batch Reactive Distillations through Conceptual Models" 16th European Symposium on Computer Aided Process Engineering, Published by Elsevier B.V (2006).
  13. Patel R., Singh K., Moses V. and Tade O. "Dynamic Simulation of Reactive Batch Distillation Column for Ethyl Acetate Synthesis" Chemical Product and Process Modeling, Vol. 2, Issue 2, Article 5 (2007).
  14. Hangx G., Kwant G., Maessen H., Markusse P., and Urseanu I. "Reaction Kinetics of the Esterification of Ethanol and Acetic Acid Towards Ethyl Acetate" Intelligent Column Internals for Reactive Separations (INTINT), Deliverable 22, Workpackage 6, Technical Report (2001).
  15. Majid S. Radhaa, Khalid A. Sukkar, Jamal M. Ali, Zaidoon M. Shakoor, and Niran Manwel "Hydrodynamics, Mass and Heat Transfer in Reactive Distillation", Al-Khwarizmi Eng. Journal, (Article in Press) (2008).
  16. Taylor, R., & Krishna, R. (1993). Multicomponent mass transfer. New York: Wiley.
  17. Peng, J., Lextrait, S., Edgar, T. F., & Eldridge, R. B. A comparison of steady-state equilibrium and rate-based models for packed reactive distillation columns. Industrial and Engineering Chemistry Research, 41, 2735-2744, (2002).
  18. R. Baur and R. Krishna Hardware selection and design aspects for reactive distillation columns. A case study on synthesis of TAME, Chem. Eng. Processing, 41, 445-462, (2002).
  19. Coulson, J. M., Richardson, J. f., "Chemical Engineering, Volume Six", 3rd ed., Pergman press company, (1978).
  20. Gmehling, J., Onken, U. and Arlt, W. "Vapor-Liquid Equilibrium Data Collection",

Eng.&Tech.Vol.26,No.7,2008

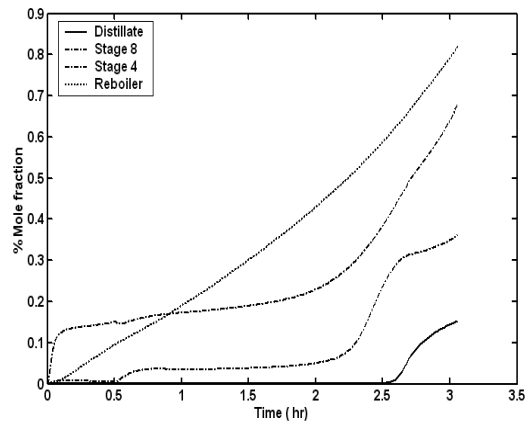
Vol. I/1-8. DECHEMA  
Chemistry Data Series.  
Frankfurt/Main,  
Germany,(1997).

Dynamic Simulation of Semi-  
Batch Catalytic Distillation  
Used for Esterification Reaction  
21. Perry, R. H. and Chilton, C.  
W. "Chemical Engineers  
Handbook", Seventh ed., New  
York: McGraw-Hill(1997)  
(1997

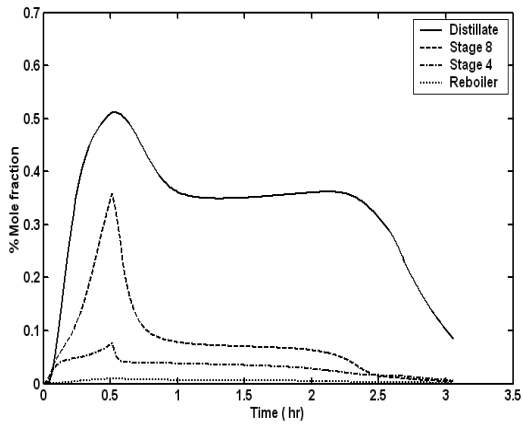
<b>NOMENCLATURE</b>		
<b>Symbol</b>	<b>Definition</b>	<b>Units</b>
$C_p$	: Specific heat	J/mol·K
$D$	: Distillate molar flowrate	mol/hr
$E$	: Activation energy	kJ/mol
$h$	: Enthalpy of a liquid mixture	J/mol
$H$	: Enthalpy of a vapor mixture	J/mol
$P$	: Total pressure	kPa
$P_i$	: Vapor pressure	kPa
$K$	: Vapour-liquid equilibrium	-
$K_{eq}$	: Reaction equilibrium constant	-
$K_1, K_2$	: Reaction rate constants	mol/(s. gm catalyst)
$L$	: Liquid flow rate	mol/hr
$M$	: Molar holdup	mol
$n$	: Number of stages	-
$Q$	: Reboiler heat duty	Watt
$R$	: Reflux ratio	-
$R_1, R_2$	: Forward and reverse reaction rate	mol/(s. gm catalyst)
$T$	: Temperature	K
$t$	: Time	hr
$V$	: Vapor flow rate	mol/hr
$W$	: Catalyst weight	gm
$x$	: Liquid mole fraction	-
$y$	: Vapor mole fraction	-
<b>Greek letters</b>		
$\epsilon$	: Void fraction of the packing	-
$\Delta H_R$	: Heat of reaction	J/mol
$\gamma_i$	: $\gamma_i$ liquid phase activity coefficient	-
<b>Subscripts</b>		
$i$	: $i$ component index	-
$n$	: Segment (stage) index	-
$L$	: Liquid phase	-
$V$	: Vapour phase	-
<b>Abbreviation</b>		
AcOH	: Acetic acid	-
DAE	: Differential algebraic equations	-
EtAc	: Ethyl acetate	-
EtOH	: Ethanol	-
H <sub>2</sub> O	: Water	-



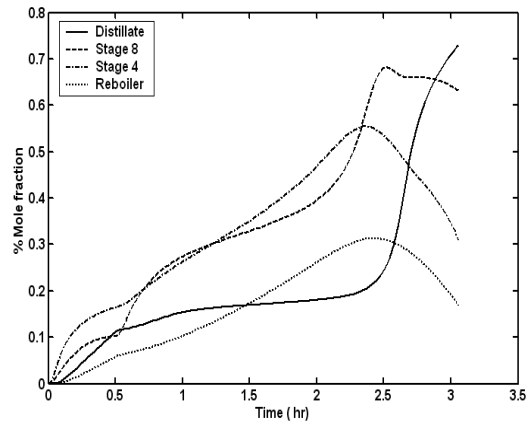
Fig(3) Mol fraction of ethanol on stages with respect to time



Fig(4) Mol fraction of acetic acid on plates with respect to time

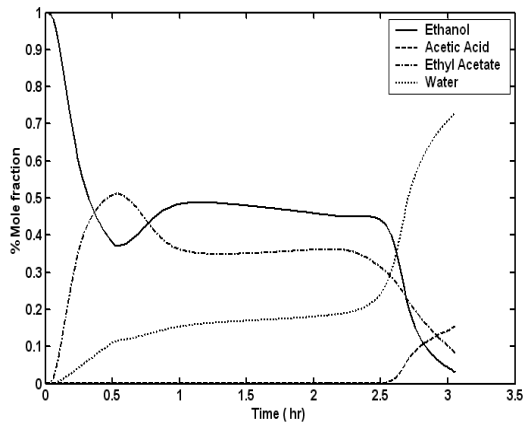


Fig(5) Mol fraction of ethyl acetate on plates with respect to time

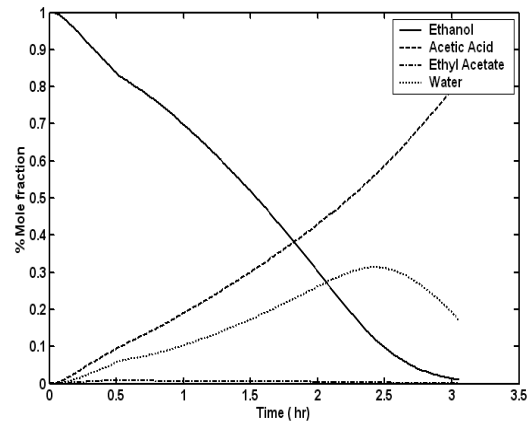


Fig(6) Mol fraction of water on plates with respect to time

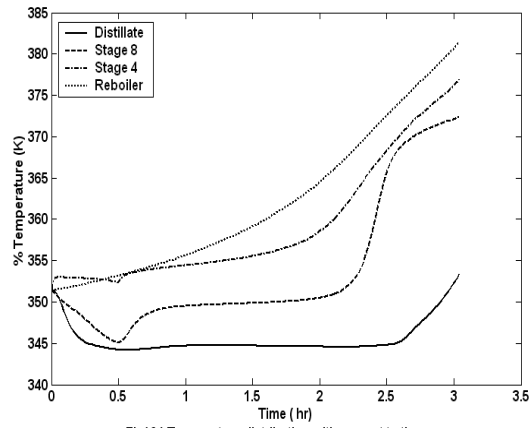




Fig(7) Mol fractions in distillate with respect to time



Fig(8) Mol fraction in reboiler with respect to time



Fig(9) Temperature distribution with respect to time

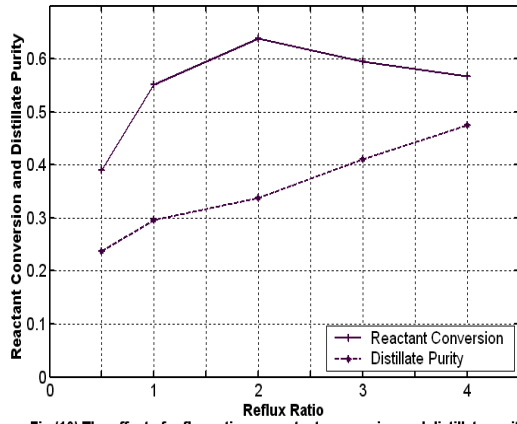


Fig.(10) The effect of reflux ratio on reactant conversion and distillate purity

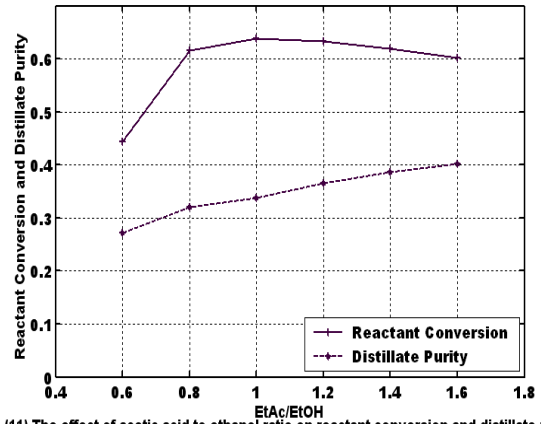


Fig.(11) The effect of acetic acid to ethanol ratio on reactant conversion and distillate purity

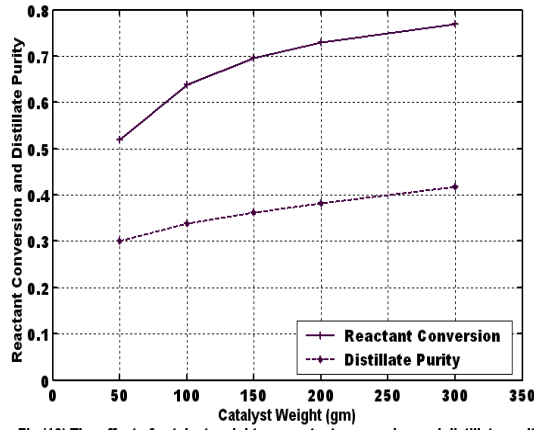


Fig.(12) The effect of catalyst weight on reactant conversion and distillate purity

Table (1) Physical Properties [19]

Component	Density (kg/m <sup>3</sup> )	Molecular weight (gm/gmol)	Boiling Point (°C)	Latent heat (J/mol)
Ethanol	789	46.069	78.35	38770
Acetic acid	1094	60.052	117.9	23697
Ethyl acetate	901	88.107	77.1	32238
Water	998	18.016	100	40683

**Table (2) Constants of NRTL Model for Ethanol(1), Acetic Acid(2), Ethyl Acetate(3),Water (4) mixture [20].**

A <sub>ij</sub> values				B <sub>ij</sub> values			
A <sub>11</sub> = 0.0	A <sub>12</sub> =0.0	A <sub>13</sub> = 1.817306	A <sub>14</sub> = 0.806535	B <sub>11</sub> = 0.0	B <sub>12</sub> = 225.4756	B <sub>13</sub> = - 421.289	B <sub>14</sub> = - 266.533
A <sub>21</sub> = 0.0	A <sub>22</sub> = 0.0	A <sub>23</sub> = 0.0	A <sub>24</sub> = - 1.9763	B <sub>21</sub> = - 252.482	B <sub>22</sub> = 0.0	B <sub>23</sub> = - 235.279	B <sub>24</sub> =609.886
A <sub>31</sub> = - 4.41293	A <sub>32</sub> =0.0	A <sub>33</sub> =0.0	A <sub>34</sub> = - 2.34561	B <sub>31</sub> =1614.287	B <sub>32</sub> =515.8212	B <sub>33</sub> =0.0	B <sub>34</sub> =1290.464
A <sub>41</sub> = 0.514283	A <sub>42</sub> =3.32933	A <sub>43</sub> =3.853826	A <sub>44</sub> =0.0	B <sub>41</sub> =444.8857	B <sub>42</sub> = - 723.888	B <sub>43</sub> = - 4.42868	B <sub>44</sub> =0.0

**Table (3) Constants of Antoine Equation for Ethanol-Water-Ethylene Glycol System [19].**

$$\ln(P^s) = C_1 + \frac{C_2}{T} + C_3 \log(T) + C_4 T^{C_5}$$

Component	c <sub>1</sub>	c <sub>2</sub>	c <sub>3</sub>	c <sub>4</sub>	c <sub>5</sub>
Ethanol	73.304	-7122.3	-7.1424	2.8853e-6	2
Acetic acid	53.27	-6304.5	-4.2985	8.8865e-18	6
Ethyl acetate	66.824	-6227.6	-6.41	1.7914e-17	6
Water	73.649	-7258.2	-7.3037	4.1653e-6	2

**Table (4) Vapor and Liquid Enthalpy Calculation [21].**

Vapor Specific Heat $Cp^v = C_1 + C_2T + C_3T^2 + C_4T^3$ $Cp^v$ in J/mol.k T in K					
<b>Component</b>	$c_1$	$c_2$	$c_3 \times 10^4$	$c_4 \times 10^8$	
Ethanol	9.014	0.214	-0.839	0.1373	
Acetic acid	4.84	0.2548	-1.753	4.948	
Ethyl acetate	7.235	0.4071	-2.091	2.854	
Water	32.243	0.001923	0.1055	-0.3596	
Liquid Specific Heat $Cp^L = C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4$ $Cp^L$ in J/mol.k T in K					
<b>Component</b>	$c_1 \times 10^{-2}$	$c_2$	$c_3 \times 10^3$	$c_4 \times 10^5$	$c_5 \times 10^9$
Ethanol	1.0264	-	-	0.2038	0.0
Acetic acid	1.396	-	0.8985	0.0	0.0
Ethyl acetate	2.2623	-	1.472	0.0	0.0
Water	2.7637	-	8.125	-	9.3701

**Table (5) Kinetic parameters for ethyl acetate formation and hydrolysis on Purolite CT179.**

K <sub>1,0</sub>	4.24×10 <sup>6</sup>	mol/kgcat.s
K <sub>2,0</sub>	4.55×10 <sup>8</sup>	mol/kgcat.s
EA,1	48.3	kJ/mol
EA,2	66.	kJ/mol

**Table (6) Semi-Batch Reactive Distillation Column Specification.**

No. of packed column stages	10
Packing height	150 cm
Rectifying section	15 cm
Reactive section	75 cm,
Stripping section	60 cm
Column diameter	2.5 cm
Condenser holdup	28.3 cm <sup>3</sup>
Reboiler holdup	2000 cm <sup>3</sup>
Catalyst location in packing column	15-75 cm
Ethyl acetate feed location in packing column	75 cm
Acetic acid feed period	2 hr
Packing type	hollow cylinder glass
Packing dimensions	L=10 mm , I D=4 mm , OD=5mm
Catalyst type	Cation, Purolite CT179
Startup period	0.5 hr
Ethanol holdup in reboiler initially	17.13 mol
Reboiler heat duty	400 Watt
Catalyst voidage	40 %
Backing voidage	60 %

**Table (7) Dynamic simulation conditions and results.**

Experiment No.	Reflux Ratio	EtAc/EtOH	Catalyst Weight	Acetic acid produced	Distillate concentration	Conversion	Time (hr)
1	0.5	1	100	6.6881	0.2371	0.3905	1.6264
2	1	1	100	9.4357	0.2957	0.5509	2.1819
3	2	1	100	10.9436	0.338	0.639	3.0569
4	3	1	100	10.1917	0.4107	0.5951	3.0944
5	4	1	100	9.7118	0.4743	0.5671	3.1528
6	2	0.6	100	7.6128	0.2726	0.4445	2.7097
7	2	0.8	100	10.5582	0.32	0.6165	3.0986
8	2	1.2	100	10.8336	0.3648	0.6326	2.8514
9	2	1.4	100	10.6142	0.3857	0.6198	2.6861
10	2	1.6	100	10.3202	0.4021	0.6026	2.5472
11	2	1	50	8.8836	0.3007	0.5187	2.8569
12	2	1	150	11.9207	0.3618	0.696	3.0889
13	2	1	200	12.5041	0.3829	0.7301	3.0569
14	2	1	300	13.1796	0.4173	0.7695	2.9597

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