Comparison between Equilibrium Model and Rate-Based Model for Simulation of Batch Zeotropic Distillation

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Abstract

In this work two models (equilibrium and nonequilibrium) have been developed to study the dynamic behavior of multicomponent zeotropic (nonazeotropic) system in batch distillation column. The results of the two models were compared with the experimental results in order to construct and develop an improved dynamic model.

The experimental work was performed through using a batch distillation column consisting of eight bubble-cap trays. zeotropic system of Benzene, Toluene, and Ethylbenzene (B-T-EB) has been used.

The equilibrium model is based on **MESH** equations (**M**aterial, **E**quilibrium relation, **S**ummation of composition, and **H**eat balances). While the Nonequilibrium model (or Rate-Based model), is based on **MERSHQ** equations (**M**aterial, **E**nergy balances, **R**ate of mass and heat transfer, **S**ummation of composition, **H**ydrodynamic equation of pressure drop, and e**Q**uilibrium relation).

It was concluded that both models give an acceptable agreement with experimental results. But nonequilibrium model required many correlations to describe the physical properties which do not exist for all systems. Also the time required to operate the program for nonequilibrium model is more than 100 times than that required to operate equilibrium model.

Key-words Batch Distillation, Equilibrium, Nonequilibrium.

المقارنة بين الموديل المبني على توازن والموديل المبني على عدم توازن البخار والسائل لمحاكاة برج التقطير الايزوتروبي ذو الدفعات

الخلاصة

تم دراسة التصرف الديناميكي لعمود تقطير الدفعات ذو الصواني عملياً و نظرياً. الدراســـة العملية أنجزت من خلال إجراء التجارب باستخدام عمود لتقطير الدفعات يتألف من ثمان صواني فقاعية. تم استخدام نظام مؤلف من البنزين والتلوين والاثيل بنزين.

الدراسة النظرية أنجزت من خلال نوعين من الموديلات يعتمد الاول علــى معـــادلات MESH وهي مختصر لموازنة المادة وعلاقة التوازن وجمع التراكيز والطاقة ويســـمى موديـــل التوازن بينما يسمى الثاني الموديل اللامتوازن ويعتمد على معادلات MERSHQ وهي مختصر لانتقال المادة والطاقة ومعدل جريان المادة والطاقة مـــع جمـــع التراكيـــب وكـــذلك المعادلـــة الهيدرودينميكية لهبوط الضغط بالإضافة إلى علاقات التوازن.

في النهاية تم التوصل الى ان كل من الموديلين يمكن ان يصف النتائج العملية بدقة مقبولة. لاكن الموديل المبني على عدم التوازن يتطلب العديد من المعادلات لوصف الخصائص الفيزيائية حيث ان هذه المعادلات غير متوفرة لكل الانظمة كذلك الوقت الازم لعمل البرنامج اللامتـــوازن اثر من مئة مرة من الوقت الازم لعمل البرنامج المبني على التوازن.

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1. Introduction

Distillation column is one of the most common forms of separation processes in modern chemical and petroleum plants, so the problem of predicting the behavior of multistage distillation has been the basis of many studies. There are two primary approaches available in the literature of modeling distillation columns called Equilibrium and Nonequilibrium (Rate-based) models.

Batch columns can be operated in three different ways: at constant-reflux ratio (with variable distillate composition), at constant distillate composition (with variable reflux ratio), and at total reflux.

Several applications have been reported in the literature, for both simulated and experimental columns (Joseph & Brosilow, 1978; Yu & Luyben, 1988; Lang & Gilles, 1990; Mejdell & Skogestad, 1991; Baratti, Bertucco, Da Rold, & Morbidelli, 1995; Chien & Ogunnaike, 1997; Kano, Miyazaki, Hasebe, & Hashimoto, 2000). However, Quintero-Marmol, Luyben, and Georgakis (1991) and Quintiero-Marmol and Luyben (1992) compared the performances of a steady-state composition estimator, a quasi-dynamic estimator (QDE), and an extended Luenberger observer (ELO) for a ternary batch column. They found that the ELO provided the best performance. However, they noted that the observer was quite sensitive to the accuracy of assumed vapor–liquid equilibria and to the assumed initial compositions.

Han and Park (2001) used Luyben's QDE to estimate the distillate composition, and to control the estimated composition profile of a batch rectifier.

The main objectives of the present study are:
1. To construct and improve a mathematical model based on the new manner of the modeling that called nonequilibrium or rate-based model, for trayed type batch distillation column.
2. Evaluation of the performance and validity of the developed model through comparing its predictions with experimental data, also comparing the new model (Nonequilibrium) with old model (Equilibrium).

2. Equilibrium-Based Model

Over 100 years ago, the equilibrium-stage model was used to model staged separation operation. The equilibrium-stage model assumes that the vapor and liquid streams leaving a given stage are in thermodynamic equilibrium with one another (Krishnamurthy and Taylor, 1985). The column is described by a group of equations that model the equilibrium stages in a column configuration. These are known as the **MESH** equations. **MESH** stands for:

M: **M**aterial balance equations for each component and total mass.
E: **E**quilibrium equations.
S: **S**ummation equations.
H: **H**eat or energy balance equations

For a better understanding of the **MESH** equations, a schematic diagram of a general equilibrium stage is shown in figure (1).

The liquid and vapor streams (L_j and V_j) leaving each stage are assumed to be in equilibrium.

The model equations for a generic stage j and component i are represented based on the commonly used distillation equations, (Seader and Henley, 1998).

The total material balance on stage j.

$$\frac{dM_j}{dt} = L_{j-1} + V_{j+1} - (V_j + S_j^V) - (L_j + S_j^L) + F_j^L + F_j^V$$

(1)

Where, M_j is the hold up of the liquid phase on the stage.

The component material balance for component i on stage j.

$$\frac{dM_j x_{i,j}}{dt} = L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} - (V_j + S_j^V) y_{i,j}$$
$$- (L_j + S_j^L) x_{i,j} + F_j^L x_{i,j}^F + F_j^V y_{i,j}^F$$

(2)

The compositions of streams leaving a stage are in thermodynamic equilibrium. Therefore the mole fractions of component

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i in the liquid and vapor streams leaving stage j are related by the equilibrium relationship.

$$y_{i,j} = K_{i,j} x_{i,j} \tag{3}$$

Two additional equations arise from the necessity that the mole fractions of all components, in either liquid or vapor phase, sum to unity.

$$\sum_{i=1}^{c} x_{i,j} = 1 \tag{4}$$

$$\sum_{i=1}^{c} y_{i,j} = 1 \tag{5}$$

The energy balance for stage j is:

$$\frac{dM_j h_j}{dt} = L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (V_j + S_j^V) H_j$$
$$- (L_j + S_j^L) h_j + F_j^L h_j^F + F_j^V H_j^F - Q_j^L - Q_j^V \tag{6}$$

3. Nonequilibrium (Rate-Based) Model

A significant application of nonequilibrium model to tray columns for vapor-liquid contacting did not appear until the work of Waggoner and Loud, 1977. They developed a rate-based mass transport model limited to nearly ideal, close-boiling, multicomponent systems. However an energy transport equation was not included (because thermal equilibrium would be closely approximated for close boiling mixture) and the coupling of component mass transfer rates was ignored.

In 1979, Krishna and Standart showed the possibility of applying rigorous multicomponent mass and heat transfer theory to calculate simultaneous transport. The theory was further developed by Taylor and Krishna, 1993.

In 1985, Krishnamurthy and Taylor made a comprehensive extension of equilibrium-stage model to a nonequilibrium-stage computer algorithm (based on fairly general multicomponent mass and energy transport models) and they developed and tested the first rate-based model for application to tray and packed columns.

In the rate-based model, two balances one for the vapor phase and one for the liquid phase replaced the conventional mass and energy balances around each tray in equilibrium-based model. Each pair of phase balances is coupled by interface transport rates, which are assumed equal in each phase at the interface. The vapor and liquid phases need not necessarily be assumed to be totally mixed. Instead, transport rates can be based on bulk-phase mole fractions using arithmetic or logarithmic mean values of entering and exiting stream conditions. Correlations of mass-and heat-transport coefficient for contacting trays can be employed to evaluate the rate of mass and heat transport. Such correlations require predictive equations for multicomponent transport properties. Any suitable thermodynamic correlation can be used to compute interface K-values as a function of interface mole fractions, interface temperature, and tray pressure. The development of an algorithm for a rate-based model requires a comprehensive knowledge of the difficult area of coupled multicomponent mass and energy transport, (Seader, 1989).

The treatment by rate-based model provides a much better description of the performance of an actual column. The column is described by a group of equations, which are known as the **MERSHQ** equations. The **MERSHQ** equations are an extension of the **MESH** equations. **MERSHQ** stands for:

M: **M**aterial balance equations for each component in the bulk liquid and vapor phase, and across the interface.

E: **E**nergy balance equations in the bulk liquid and vapor phase, and across the interface.

R: Rate equations for mass transfer of C-1 components, plus one energy transfer rate equation.

S:**S**ummation equations or composition constraints.

H: **H**ydraulic equations for pressure drop.

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Q: e**Q**uilibrium relation at the interface.

For a better understanding of the **MERSHQ** equations, a schematic diagram of a general nonequilibrium stage is shown in Figure (2).

4 Mathematical Modeling

4.1 Assumptions of the Nonequilibrium Model

Many models concerning dynamic simulation of batch distillation were reported. But most of these models were presented with inappropriate simplifying assumptions such as vapor-liquid equilibrium, constant liquid holdup on trays, ideal vapor, negligible vapor holdup, constant molar overflow, negligible energy balance. Sometimes these assumptions make the predictions of the model far from reality when simulated with another system.

In the present study the following assumptions were proposed for the nonequilibrium model of batch distillation:

1. The vapor-liquid interface is at thermodynamic equilibrium.

2. The vapor and liquid reached to thermodynamic equilibrium on trays just at steady state in total reflux condition.

3. The trays are in mechanical equilibrium; $P_j^V = P_j^L = P_j$.

4. The mass and energy transport are from vapor phase to liquid phase.

5. The flow patterns are plug flow for vapor through perfectly mixed liquid.

6. The total molar holdup of vapor and liquid on the tray are constant during any short time interval.

7. The condenser operates at total condensation.

8. The modeling of reboiler and condenser based on equilibrium model.

9. The pressure along the column is constant due to low-pressure drop that had been measured during the experiments.

10. The walls of the column are perfectly insulated.

4.2 Nonequilibrium-Stage Model Equations

The nonequilibrium-stage model equations as below.

M. **Total and component Material balances**

The total material balances for vapor and liquid phases are:

$$\frac{dM_j^V}{dt} = V_{j-1} - V_j - N_{T,j} \qquad (7)$$

$$\frac{dM_j^L}{dt} = L_{j+1} - L_j + N_{T,j} \qquad (8)$$

The amount of liquid staying on a tray is the holdup. The liquid hold up is a function of the geometry and the type of contacting device; therefore the liquid volumetric holdup is often constant (Galindez and Fredenslund, 1988). As the liquid volumetric holdup is constant the remaining space that occupied by the vapor is constant too, i.e. the volumetric holdups of the liquid and vapor are constant on a tray. If the molar density is assumed not to vary considerably during a short interval time, the molar holdup can be assumed to remain constant during this short time interval. In fact the change in molar density does not vary considerably on any tray during short intervals of time. Thus, during short intervals of time,

$$\frac{dM_j^V}{dt} \gg \frac{dM_j^L}{dt} \gg 0 \qquad (9)$$

$$V_j = V_{j-1} - N_{T,j} \quad \text{j=2,3,…,(N-1)} \qquad (10)$$

$$L_{j+1} = L_j - N_{T,j} \quad \text{j=2,3,…,(N-1)} \qquad (11)$$

And the component material balances of component i in vapor and liquid phases on stage j are:

$$\frac{dy_{i,j}}{dt} = \frac{V_{j-1}}{M_j^V} y_{i,j-1} - \frac{V_j}{M_j^V} y_{i,j} - \frac{N_{i,j}^V}{M_j^V} \qquad (12)$$

$$\frac{dx_{i,j}}{dt} = \frac{L_{j+1}}{M_j^L} x_{i,j+1} - \frac{L_j}{M_j^L} x_{i,j} + \frac{N_{i,j}^L}{M_j^L} \qquad (13)$$

E. Energy balances

The energy balances of vapor and liquid phases on stage j are:

$$\frac{dH_j}{dt} = \frac{V_{j-1}}{M_j^V} H_{j-1} - \frac{V_j}{M_j^V} H_j - \frac{e_j^V}{M_j^V} \qquad (14)$$

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$$\frac{dh_j}{dt} = \frac{L_{j+1}}{M_j^L} h_{j+1} - \frac{L_j}{M_j^L} h_j + \frac{e_j^L}{M_j^L} \qquad (15)$$

R. Rate of mass and energy across the interface

At the vapor-liquid interface, there is no mass or energy accumulation. Thus,

$$N_{i,j}^V = N_{i,j}^L \qquad (16)$$

$$e_j^V = e_j^L \qquad (17)$$

The rate of component mass transfer across the vapor and liquid films are based on the method, where diffusive and convective (bulk-flow) contributions are included

$$(N_{i,j}^V) = (J_{i,j}^V) + (\overline{y}_{i,j})N_{T,j} \qquad (18)$$

$$(N_{i,j}^L) = (J_{i,j}^L) + (x_{i,j})N_{T,j} \qquad (19)$$

$$(J_{i,j}^V) = c_T^V [ka_{i,j}^V](\overline{y}_{i,j} - y_{i,j}^I) \qquad (20)$$

$$(J_{i,j}^L) = c_T^L [ka_{i,j}^L](x_{i,j}^I - x_{i,j}) \qquad (21)$$

$$\sum_{i=1}^c N_{i,j}^V = \sum_{i=1}^c N_{i,j}^L = N_{T,j} \qquad (22)$$

The rate of energy transfer across the vapor and liquid films is based on the convective heat transfer and the enthalpies by mass transfer contributions are included:

$$e_j^V = ha^V (T^V - T^I) + \sum_{i=1}^c N_{i,j}\overline{H}_{i,j} \qquad (23)$$

$$e_j^L = ha^L (T^I - T^L) + \sum_{i=1}^c N_{i,j}\overline{h}_{i,j} \qquad (24)$$

Heat transfer coefficients for the vapor film are estimated from the Chilton-Colburn analogy between heat and mass transfer and for the liquid phase film, a penetration model is preferred. Thus

$$ha^V = ka^V r^V Cp^V (Le^V)^{2/3} \qquad (25)$$

$$ha^L = ka^L r^L Cp^L (Le^L)^{1/2} \qquad (26)$$

S. Summation of mole fractions

The constraints summation of the mole fractions at vapor-liquid interface are:

$$\sum_{i=1}^c y_{i,j}^I = 1.0 \qquad (27)$$

$$\sum_{i=1}^c x_{i,j}^I = 1.0 \qquad (28)$$

And the normalization procedure that is used in equilibrium-stage model (Seader and Henley, 1998) will be used for mole fractions of vapor and liquid phases in present nonequilibrium-based model. Thus,

$$(y_{i,j})_{normalized} = \frac{y_{i,j}}{\sum_{i=1}^c y_{i,j}} \qquad (29)$$

$$(x_{i,j})_{normalized} = \frac{x_{i,j}}{\sum_{i=1}^c x_{i,j}} \qquad (30)$$

H. Hydraulic equation of pressure drops

The distillation column operates at atmospheric pressure. The condenser pressure is equal to atmospheric pressure, and the pressure in the reboiler is slightly higher than the condenser by an amount equal to the measured pressure drop. The measured pressure drop along the column was between 61 mm H2O (600 Pa) maximum and 56 mm H2O (550 Pa) minimum. This means that the average pressure drop was 575 Pa, which is small enough to consider the column to be operating at constant pressure.

Q. eQuilibrium equation at vapor-liquid interface

The thermodynamic equilibrium of each component was assumed to exist only at the interface:

$$y_{i,j}^I = K_{i,j}x_{i,j}^I \qquad (31)$$

4.3 Other Calculations

a) Total holdup calculation:

The model was based on constant molar holdup on trays during short intervals of time; therefore the vapor and liquid molar holdups on tray j were evaluated periodically through:

$$M_j^V = \frac{Vap.Vol.on\ tray}{\sum_{i=1}^c \frac{y_i Mwt_i}{r_i^V}} \qquad (32)$$

$$M_j^L = \frac{Liq.Vol.on\ tray}{\sum_{i=1}^c \frac{x_i Mwt_i}{r_i^L}} \qquad (33)$$

b) Enthalpy calculation

The enthalpy of vapor and liquid phases mixtures were calculated by using the following equations:

$$H_j = \sum_{i=1}^c y_{i,j}H_{i,j} \qquad (34)$$

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$$h_j = \sum_{i=1}^{c} x_{i,j} h_{i,j} \tag{35}$$

c) Equilibrium relation calculation

At the vapor-liquid interface, a thermodynamic equilibrium is assumed to be established and the following relation relates the composition of component in vapor phase with the composition of component in liquid phase on tray j:

$$y_{i,j}^I = K_{i,j} x_{i,j}^I \tag{36}$$

Where,

$$K_{i,j} = \frac{P_{i,j}^o}{P} \frac{g_{i,j}}{\hat{f}_{i,j}^v} \tag{37}$$

Where, $P_{i,j}^o$ is the vapor pressure of component i on tray j and its value is function of temperature and component constant parameters according to Antoine's equation that used to find the vapor pressure values.

$$ln\, P_i^o = A_i - \frac{B_i}{T + C_i} \tag{38}$$

The UNIQUAQ model was used to evaluate the activity coefficient for liquid phase $g_{i,j}$ in the present simulation.

For evaluating of the component fugacity coefficient in the vapor phase $\hat{f}_{i,j}^v$, two models had been compared, (Virial equation, and Redlich/Kwong equation). Virial equation is implemented in the present modeling the values that have been predicted form these two models are very close and they are rarely, below 0.95 (Ibrahim, 2007).

4.4 Modeling of Reboiler and Condenser

Distillation columns have various types of condensers and reboilers that usually have a significantly larger holdup, especially the reboiler, than the holdup on any tray to give the column operational stability. Larger holdups lead to differences in the transient behavior of various variables and, therefore, have a large effect on the column behavior. They also cause the system of equations to be stiff.

The reviewed literatures dealing with nonequilibrium model have used equilibrium-based model for both the reboiler and condenser. The equilibrium-based model will therefore be used in the present modeling for reboiler and condenser.

4.4.1 The Reboiler Model

The reboiler assumed as the first tray in the distillation column. The **MESH** equations are used for modeling the reboiler, where the total material balance is:

$$\frac{dM_1^L}{dt} = L_2 - V_1 \approx \frac{DM_1^L}{Dt} \approx \frac{M_1^L(t + Dt) - M_1^L(t)}{Dt} \tag{39}$$

Where M_1^L is the total liquid holdup, whose quantity decreases continuously during the production period of the batch operation. The variation of the total liquid molar holdup in the reboiler is:

$$M_1^L(t) = M_1^o - \sum_{j=2}^{10} M_j^L - \sum_{j=2}^{9} M_j^V - \int_0^t D dt \tag{40}$$

Where M_1^o is the initial charge to the reboiler.

A component material balance is:

$$\frac{dM_1^L x_{i,1}}{dt} = L_2 x_{i,2} - V_1 y_{i,1} \tag{41}$$

The liquid and vapor were assumed in thermodynamic equilibrium conditions.

$$y_{i,1} = K_{i,1} x_{i,1} \tag{42}$$

By expanding the first term of equation (41) and substituting equation (39), and equation (38), by this equation and rearranging, gives;

$$\frac{dx_{i,1}}{dt} = \frac{L_2}{M_1^L} x_{i,2} - \left(\frac{L_2 + V_1(K_{i,1} - 1)}{M_1^L} \right) x_{i,1} \tag{43}$$

The energy balance is:

$$\frac{dM_1^L h_1}{dt} = L_2 h_2 - V_1 H_1 + Q_B \tag{44}$$

By expanding the first term of the last equation and substituting equation (39) by equation (44) the resulting equation is:

$$\frac{dh_1}{dt} = \frac{L_2}{M_1^L}(h_2 - h_1) - \frac{V_1}{M_1^L} l_1 + \frac{Q_B}{M_1^L} \tag{45}$$

A rearrangement gives:

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$$V_1 = \frac{L_2(h_2 - h_1) + Q_B - M_1^L \frac{Dh_1}{Dt}}{l_1}$$

Substituting equation (39) by the last equation to eliminate the liquid flow rate, gives:

$$V_1 = \frac{\frac{DM_1^L}{Dt}(h_2 - h_1) + Q_B - M_1^L \frac{Dh_1}{Dt}}{l_1 - (h_2 - h_1)}$$

(46)

Where, $l_1 = H_1 - h_1$, and

$$\frac{dh_1}{dt} \gg \frac{Dh_1}{Dt} \gg \frac{h_1(t + Dt) - h_1(t)}{Dt}$$

Summation equations for vapor and liquid phases are also considered. Thus,

$$\overset{c}{\underset{i=1}{\textstyle\sum}} x_{i,1} = 1$$

(47)

$$\overset{c}{\underset{i=1}{\textstyle\sum}} y_{i,1} = \overset{c}{\underset{i=1}{\textstyle\sum}} K_{i,1} x_{i,1} = 1$$

(48)

The liquid mixture in the reboiler is assumed always to be at bubble point, so that equation (48) will solved by trial and error technique to evaluate the bubble point temperature and the values of $K_{i,1}$.

4.4.2 The Condenser Model

The condenser represents the last tray of the column. The condenser is operated at total condensation, the total and component material balances are:

$$\frac{dM_{10}^L}{dt} = V_9 - (L_{10} + D) \gg \frac{DM_{10}^L}{Dt}$$

(49)

Where, M_{10}^L is the total liquid holdup, and D is the distillate.

$$\frac{dM_{10}^L x_{i,10}}{dt} = V_9 y_{i,9} - L_{10} x_{i,10} - D x_{i,D}$$

(50)

Where

$$x_{i,10} = x_{i,D}$$ (51)

By expanding the first term of equation (50) and substituting equation (49) and the equality equation (51) by this equation and then rearranging, gives;

$$\frac{dx_{i,10}}{dt} = \frac{V_9}{M_{10}^L}(y_{i,9} - x_{i,D})$$ (52)

The energy balance is:

$$\frac{dM_{10}^L h_{10}}{dt} = V_9 H_9 - L_{10} h_{10} - D h_D - Q_C$$

(53)

Also by expanding the first term of equation (53) and substituting equation (49) and by equality $h_{10} = h_D$ by this equation, rearranging the resulting equation will be:

$$Q_C = V_9 l_{10} - M_{10}^L \frac{Dh_{10}}{Dt}$$

(54)

Where, $l_{10} = H_9 - h_{10}$

The condenser is operating at total condensation, and the liquid stream that exits from the condenser $(L_{10} + D)$ is assumed to be saturated liquid i.e. the liquid in the condenser is at bubble point temperature of its mixture. Thus;

$$\overset{c}{\underset{i=1}{\textstyle\sum}} K_{i,D} x_{i,D} = 1$$

(55)

To determine the values of $K_{i,D}$, the same technique of bubble point calculation used for the reboiler model will be used here.

The batch distillation column was operating at a constant reflux ratio, so that the reflux ratio R is in advance specified variable. Where,

$$R = \frac{L_{10}}{D}$$

(56)

4.5 Physical Properties

The successful implementation of a column solver requires more than "just solving" the equations. A large and important part of a process simulator are the physical property models which supply the K-values, activity coefficients, binary diffusivities, densities, heat capacities, enthalpies, vapor pressures, viscosities, thermal conductivities, surface tensions, and binary mass transfer coefficients. A nonequilibrium model has a much higher demand for properties compared to an equilibrium model (Taylor et al., 1994, and 2003).

Table (1) identifies the major physical properties requirements. It is obvious that

nonequilibrium models are more demanding of physical property data than are equilibrium stage models (except when tray-efficiency and equipment design calculations are carried out, but those are done after simulation and are not needed to carry out the column simulation) (Taylor et al., 2003).

5. Solution Procedure
5.1 Equilibrium Model

Figure (3) shows the flowchart for the solution steps of equilibrium stage model to simulate batch distillation column. This algorithm can be applied to calculate the temperature, liquid flowrate, vapor flowrate and the composition profiles for a column containing a known number of stages. Initially, the vapor flowrates and liquid are equal to the still vapor flowarte.

The input parameters needed in simulation program are: reflux ratio, number of plates, heat duty in reboiler, initial charge in reboiler, hold-up on plates, hold-up in condenser, and the initial concentration on plates an in reboiler.

In this model the equilibrium stage model equations (1 to 6) are solved simultaneously with the equations of both reboiler and condenser (eqs 39 to 59)

5.2 Non-equilibrium Model

The procedure of performing the batch distillation calculations involves simultaneous solution of ordinary differential equations and algebraic equations, starting from the initial state of the column.

The first and the important step in the solution procedure is the evaluation of the composition profile of all components along the column at a steady state conditions at total reflux operation. This is because the solution of the present model is initialized with these values for the solution of components material balances (solution of initial value problem of ODE). The liquid temperatures of all stages at steady state condition in total reflux are assumed to be the bubble points of the liquid mixtures at these stages and the vapor temperatures are assumed to be the dew points of the vapor mixtures. The evaluation of the bubble point was based on the estimation of steady state composition.

The estimation of the composition profile at steady state that is used to initialize the present model is based on the shortcut method of Kim and Ju, 1999. This shortcut method was based on equilibrium-stage model, and the authors applied this method on the laboratory scale trayed batch distillation to a system of benzene, toluene, o-xylene, which is similar to the system studied in the present work. This method showed a very good agreement for the prediction of steady state compositions.

The solutions of the reboiler, trays, and condenser models were integrated together to give the present nonequilibrium-based model, where $2C+5$ variables in reboiler, $6Cn +10n$ variables in trays (n=number of trays), and $C+5$ in the condenser. The total number of variables for nonequilibrium model are $6Cn+3C+10n+10$ where (C: No. of components, and n: No. of trays) which are equal to 243 variables for the present study. The number of equations are $6Cn+3C+10n+10 = 243$ too. Only 70 of these equations $2(Cn+C+n) = 70$ are ODE and the rest $4Cn+C+8n+10 = 173$ are AE. The total number of equations is $(5C+10)$ per general stage where C represents the number of components in the system. Out of these, $(2C+2)$ equations are ordinary differential equations while the rest $(3C+8)$ are algebraic equations.

A serious computational problem occurs when integrating the ODE of batch distillation because the liquid holdups on trays and in the condenser are small. The values of corresponding vapor and liquid mole fractions $y_{i,j}$, and $x_{i,j}$ respond are quickly to changes. The opposite holds for the reboiler (still) with its large liquid holdup. Hence, the required time step for accuracy is usually small, leading to a very slow response of the overall system.

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Systems of ODE having this characteristic are so-called stiff systems (Carnahan and Wilkes 1981).

All other equations, correlations and physical properties about (B-T-EB) system is found in Ibrahim, 2007.

In the present dynamic model the solution of the ODE are based on the solvers build-in MATLAB software. MATLAB provides several powerful approaches to integrate sets of ODE of initial value problems. MATLAB-type methods strive for accuracy, stability, and computational efficiency by using one and multistep variable order, and variable step-time implicit techniques. The details of MATLAB solvers for the initial value problems of ODE, their specifications and algorithms are given in (Ibrahim, 2007). Of these solvers code [ode15s] was used in the present model.

Figure (4) shows the flowchart for the solution steps of non-equilibrium stage model to simulate batch distillation column.

6. Experimental Distillation Column

The experiments were carried out using a laboratory scale batch distillation column shown as a photograph in Figure (5). The distillation column consists of a still pot, which is heated by using a heating mantle. The column is located above the still pot, and consists of eight bubble-cap trays, each one equipped with sampling valve and thermocouple sensor. At the top of the column, a double-pipe condenser is connected, which is used to condense the vapor leaving the top of the column. Another double-pipe condenser located prior to the distillate collection pot is used to ensure that there is no vapor exit as product and cool the distillate. A magnetic reflux unit (solenoid valve) situated near the top of the column controls the rate of condensate being sent to distillate collection pot.

The distillation column is manufactured from a heat resistant glass, and fitted with a glass jacket plated with a double vision fringe in order to reduce heat losses as far as possible. The main column, of 1 m height and 8.1 cm inner diameter, consists of eight bubble-cap trays of 30 cm^3 liquid holdup for each tray and a glass valve connected at the liquid zone of each tray for sampling. There is a thermocouple sensor on each tray for measuring temperature.

The column is connected at the lower part to a 2 liters capacity spherical heat resistant glass vessel with four open necks for installing instruments, as well as a sampling valve. The still pot is equipped with 500 Watt electrical heating mantle. The electrical heater power is regulated by an interface unit connected to a personal computer.

7. Comparison of Nonequilibrium Model and Equilibrium Model with Present Experimental Data

The system used in the present work (B-T-EB) is considered as a wide-boiling point system (80.1, 110.6, and 136.1ºC) respectively, it is also considered as zeotropic system.

The predictions of the dynamic compositions of (B-T-EB) system obtained from the present nonequilibrium-based model and that obtained from the equilibrium-based model by Shakoor, 2004, were compared with the present experimental data of ordinary batch distillation of B-T-EB system in order to give more evaluation for the performance of the present model.

All experimental data that are carried out in the present experimental work (Table 3) were used for this comparison. Results of the comparison are shown in Figures (6) to (11).

The equilibrium-based model by Shakoor, as compared with the present nonequilibrium-based model, was constructed based on the following: -
1. Neglecting tray efficiency.
2. Neglecting vapor holdup.
3. Neglecting the heat of formation of all components by setting the enthalpy of all

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liquid components to zero at 298 K.

4. Constant physical properties.

5. Using Newton's method for calculating bubble point by neglecting the change of liquid activity coefficient with temperature.

6. The calculation started for all stages with the same initial charge composition of the still.

7. The attending of steady state in total reflux condition after a specified period of time (0.5 hour in present simulation).

In spite of all these assumptions the predictions of Shakoor's model was good with respect to the present experimental data as shown in Figures (6) to (11) and occasionally in some points the predictions of this model was better than that of the present model. However, these figures indicate that the predictions of the present model are significantly better than that of the equilibrium-based model. This conclusion is supported by the statistical parameters and relative performance factor as given in the following section.

Figures (6 to 11) contain plots of experimental and simulation results of equilibrium and nonequilibrium models respectively with Table (3). It's clear from these six figures that there good agreement between both simulation results and experimental results especially in the behavior of distillate, tray 5 and still with time.

By using Pentium 4 computer with 1.6 GHz CPU, the time required to operate the nonequilibrium model program is 8 to 10 hours depending on selected operating conditions, while the time required to operate the equilibrium model program is 5-7 minutes. In all experiments the time of operation of the nonequilibrium model program is more than the time required for the experiment.

7.1 Criteria for Comparing the Models With Experimental Data

To evaluate the two models the models results are compared with the experimental results for all time range. The evaluation is based on the following statistical parameters (Ansari et al., 1994).

1. Average Percent Error*:*

$$E_1 = \left(\frac{1}{N} \sum_{i=1}^{N} Er_i\right) \times 100 \qquad (57)$$

where,

$$Er_i = \frac{x(pred.) - x(meas.)}{x(meas.)} \qquad (58)$$

(E_1) indicates the overall trend of the performance, relative to the measured mole fraction.

2. Absolute Average Percentage Error:

$$E_2 = \left(\frac{1}{N} \sum_{i=1}^{N} |Er_i|\right) \times 100 \qquad (59)$$

(E_2) indicates how large the errors are on the average.

3. Percent Standard Deviation:

$$E_3 = \left(\sum_{i=1}^{N} \sqrt{\frac{(Er_i - E_1)^2}{N-1}}\right) \qquad (60)$$

(E_3) indicates the degree of scattering of the errors over their average value.

4. Average Error:

$$E_4 = \left(\frac{1}{N} \sum_{i=1}^{N} Er_i'\right) \qquad (61)$$

where,

$$Er_i' = x(pred.) - x(meas.)$$

(62)

(E_4) indicates the overall trend independent of the measured mole fraction.

5. Absolute Average Error:

$$E_5 = \left(\frac{1}{N} \sum_{i=1}^{N} |Er_i'|\right) \qquad (63)$$

(E_5) is also independent of the measured mole fraction and indicates the magnitude of the average error.

6. Standard Deviation:

$$E_6 = \sum_{i=1}^{N} \sqrt{\frac{(Er_i' - E_4)^2}{N-1}} \qquad (64)$$

(E_6) indicates the scattering of the results, independent of the mole fraction.

It's clear from Table (4) which contains statistical results for the evaluation of models, that the nonequilibrium model is better than equilibrium model in some type

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of error while the equilibrium is better in others.

6. Conclusion

The dynamic simulation models of distillation columns consist of a system of equations based on mass and energy balances around each plate of the column as well as reboiler and condenser. Typically for the dynamic problems, these balances lead to system of ordinary differential equations (ODE) or to mixed system of ordinary differential equations and Algebraic equations (DAE), which are solved by a suitable integration method. The set of nonlinear ordinary differential equations governing the unsteady state composition and temperature profiles and the set of algebraic equations of mass and energy transfer, and thermodynamic calculations were solved numerically in these two models to give the dynamic compositions and temperature profiles in trays along the column as well as the the internal liquid and vapor flow rates, the holdups in the column and the instant product rate with its composition.

1. Both equilibrium model and nonequilibrium model could be used to simulate batch azeotopic distillation.

2. The time required to simulate a non-ideal system with nonequilibrium model in a computer required few hours while in the case of equilibrium model few minutes.

3. Both models could be able to predict the dynamic behavior of the followings:

- Liquid and vapor compositions profiles.
- Liquid and vapor temperature profile.
- Liquid and vapor internal flow rates.
- Distillate flowrate, and composition.
- Stage holdup profile.

NOMENCLATURE

Symbol	Definition
a	Interfacial area (-)
C	Number of component
D	Distillate molar flowrate (mol/s)
Cp	Specific heat capacity (J/mol.K)
c_T	Total molar concentration (mol/m^3)
e	Energy transfer rate (Watt)
Er	Error or prescribed tolerance
F	Feed molar rate (mole/s)
H	Vapor molar enthalpy (mole/s)
Ĥ	Total energy summation (mole/s)
h	Heat transfer coefficient (W/m^2.K)
h	Liquid molar enthalpy (mole/s)
i	Component identification number
j	Stage identification number
K	Vaporization K-value
L	Liquid molar load on each stage (mol/s)
l	Component molar rate (mole/s)
J	Molar flux by ordinary molecular diffusion relative to molar average velocity of the mixture (mol/m^2.s)
K	Thermodynamic equilibrium constant (-)
k	Mass transfer coefficient (m/s)
κ	Binary pair mass transfer coefficient (m/s)
k	Thermal conductivity (W/m.K)
M	Molar holdup (mol)
N	Mass transfer rate (mol/s)
N	Number of stages
P	Column Pressure (kPa)
P°	Vapor pressure (kPa)
ΔP	Pressure drop (kPa)
Q	Rate of heat transfer (J/s)
S	Entropy (J/mol.K)
T	Temperature (K)
V	Vapor molar load on each tray (mol/s)
X	Liquid mole fraction
Y	Vapor mole fraction

Greek Symbols

γ	Liquid activity coefficient
φ	Fugacity
λ	Latent heat of vaporization (J/mol)
r	Density (kg/m^3)

Sub- and Superscripts

B	Reboiler
C	Condenser
F	Feed
i	Component i
j	Plate j
ij	Component I in plate j
T	Total
L	Liquid phase
V	Vapor phase

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Table (1): Physical Properties Required for Equilibrium and Nonequilibrium Models.

Nonequilibrium Model	Equilibrium Model
Activity Coefficients Vapor Pressures Fugacity Coefficients Densities Enthalpies Diffusivities Viscosities Surface Tension Thermal Conductivities Mass-Transfer Coefficients Heat-Transfer Coefficients	Activity Coefficients Vapor Pressures Fugacity Coefficients Densities Enthalpies

Table (2): Variables and Equations for the Dynamic Nonequilibrium Tray Model

Variable	Number	Differential
V_j	1	No
L_j	1	No
M_j^V	1	No
M_j^L	1	No
$y_{i,j}$	C	Yes
$x_{i,j}$	C	Yes
H_j	1	Yes
h_j	1	Yes
T_j^V	1	No
T_j^L	1	No
T_j^I	1	No

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$y^I_{i,j}$	C	No
$x^I_{i,j}$	C	No
$N_{i,j}$	C	No
$N_{T,j}$	1	No
Total Number of Variables per Stage		5C+10

Table (3): The Studied Operating Conditions for the Experimental Work.

Exp. No.	Initial Still Composition (mole fraction)			Reflux Ratio	Heat Duty (Watt)
	Benzene	Toluene	Ethylbenzene		
1	0.3	0.4	0.3	1	336
2	0.3	0.4	0.3	2	336
3	0.3	0.4	0.3	4	336
4	0.3	0.4	0.3	4	222
5	0.2	0.3	0.5	4	336
6	0.5	0.3	0.2	4	336

Table (4): The statistic results for the evaluation of models.

Model	Nonequilibrium	Equilibrium
E_1	-9.5519	-8.6586
E_2	42.4901	72.5979
E_3	139.3021	126.2747
E_4	6.302×10^{-10}	-1.080×10^{-06}
E_5	0.0464	0.0974
E_6	0.0032	0.0067

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Figure (1): General Equilibrium Stage Model

Figure (2): General Nonequilibrium Stage Model

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                                                   Zeotropic Distillation

Start

Read column data

Input initial column composition

Input total time

Time =Time+ΔTime

If Time < S.S time → Reflux ratio = ∞

No

Reflux ratio = value

Calculate bubble point of each tray using Newton-Raphson method

Calculate K values for trays, condenser and rebolier

Calculate liquid holdup

Integrate Jacobian matrix

Calculate new compositions on trays, condenser and reboiler

Normalize the compositions on trays, condenser and reboiler

Calculate liquid and vapor enthalpys

Evaluate the enthalpy and total mass derivatives

Solve enthalpy and total mass derivatives by using finite element method

Update liquid and vapor internal flowrates

No ← If Time ≥ Total time

Yes

Plot the results

Stop

Figure (3): The Flow Chart of Solution Steps of equilibrium Stage Model

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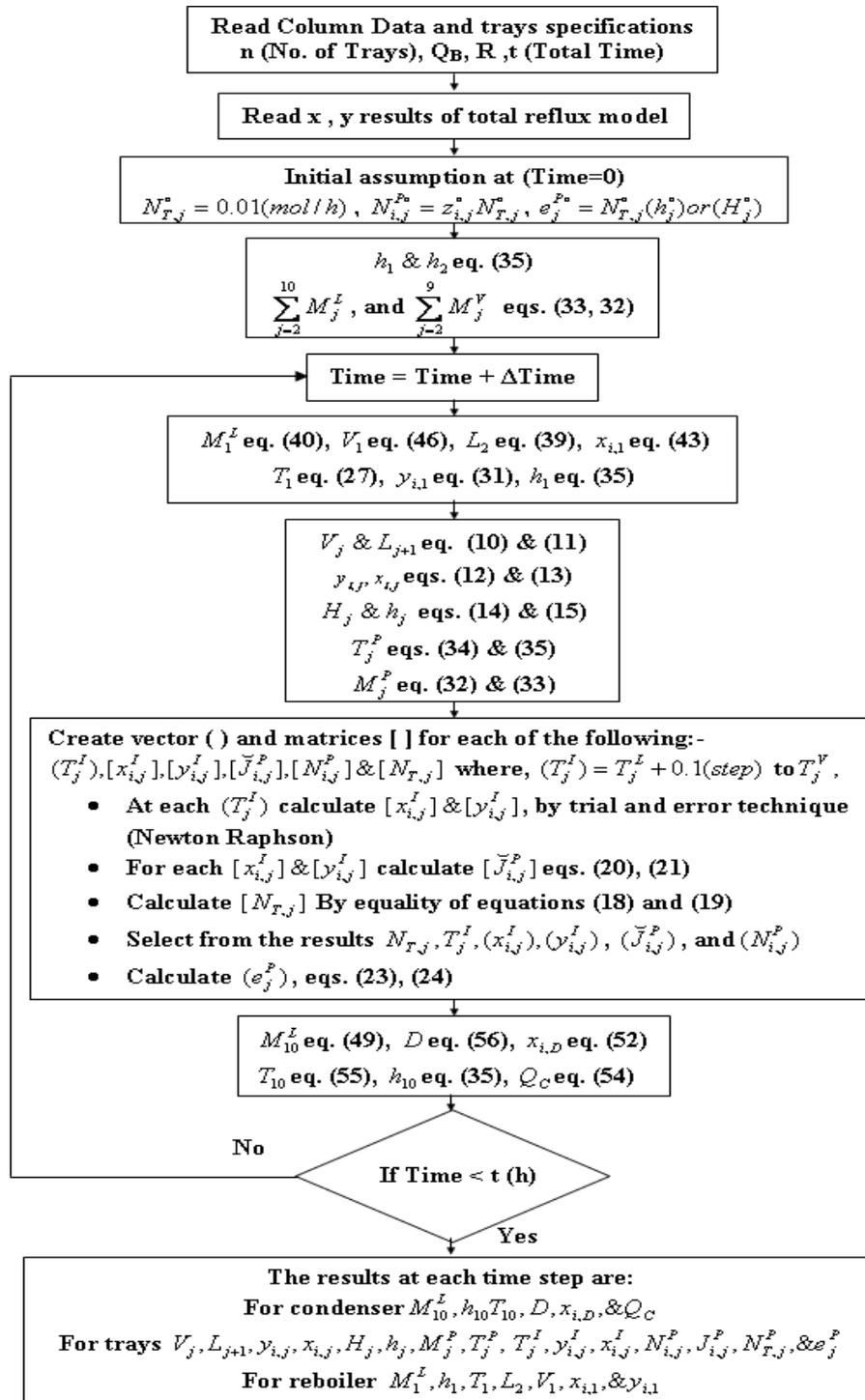
Figure (4): The Flow Chart of Solution Steps of Non-equilibrium Stage Model

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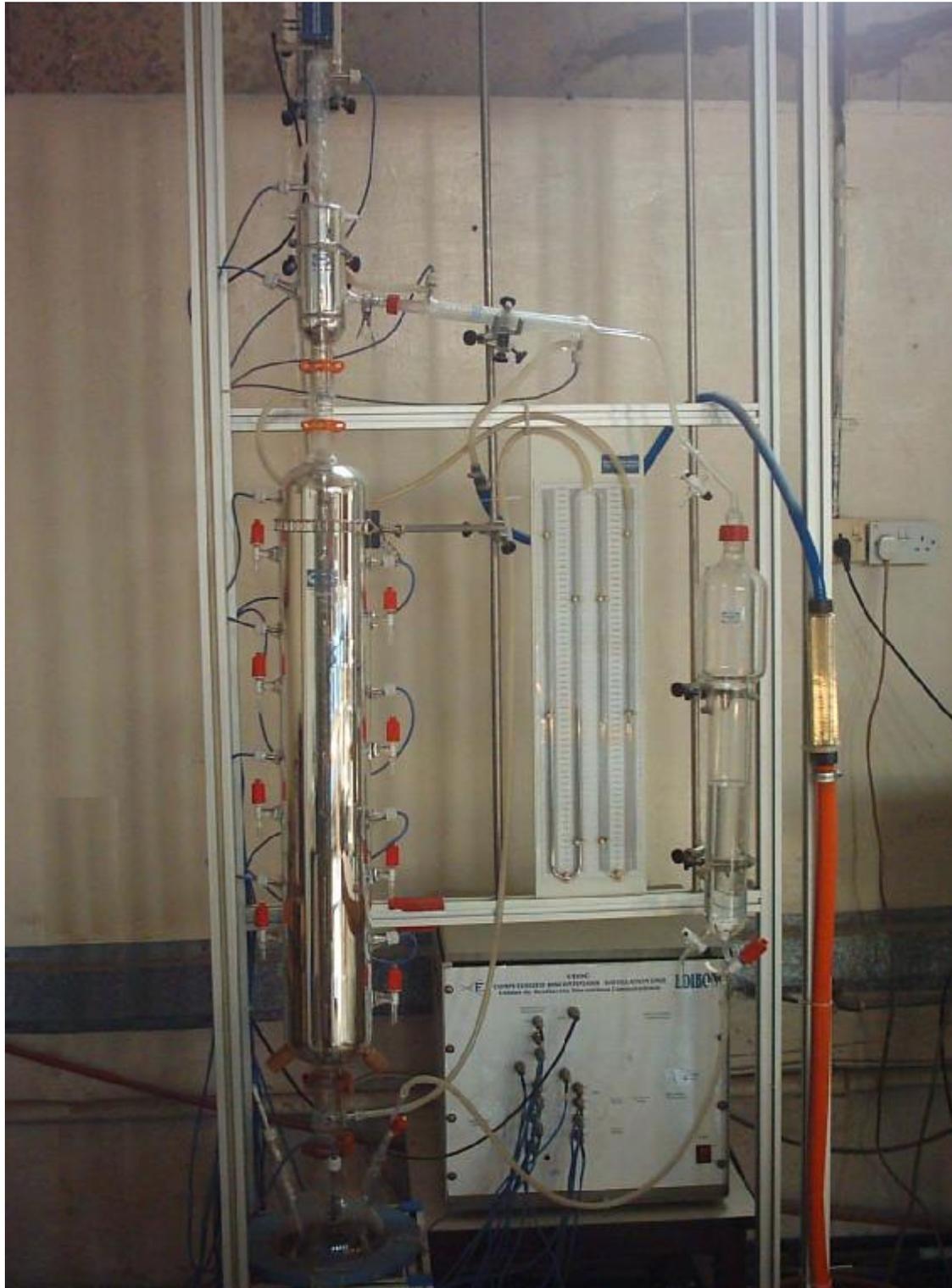
Figure (5): Photograph for The Experimental Rig of Batch Distillation Column

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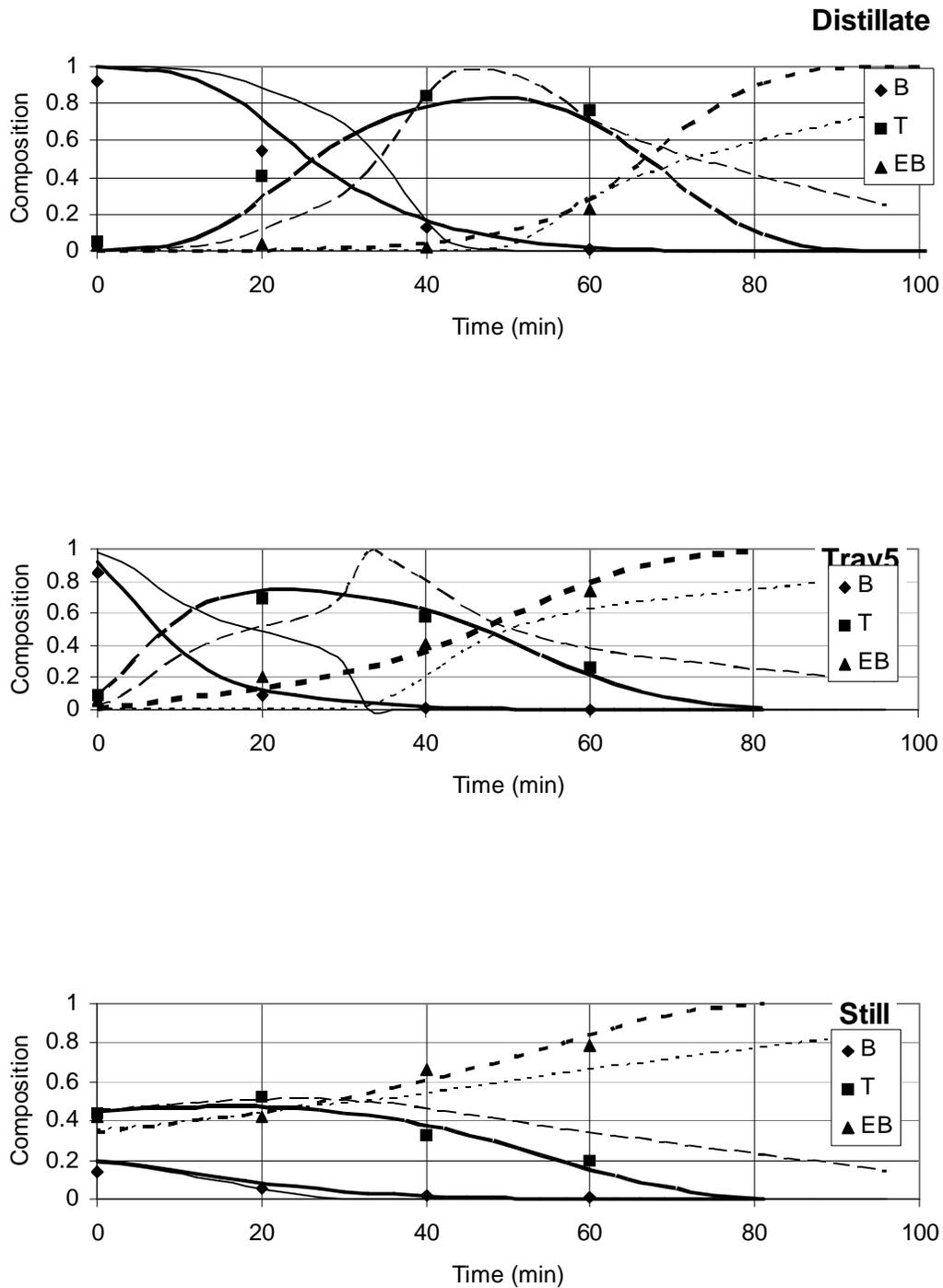Rate-Based Model for Simulation of Batch
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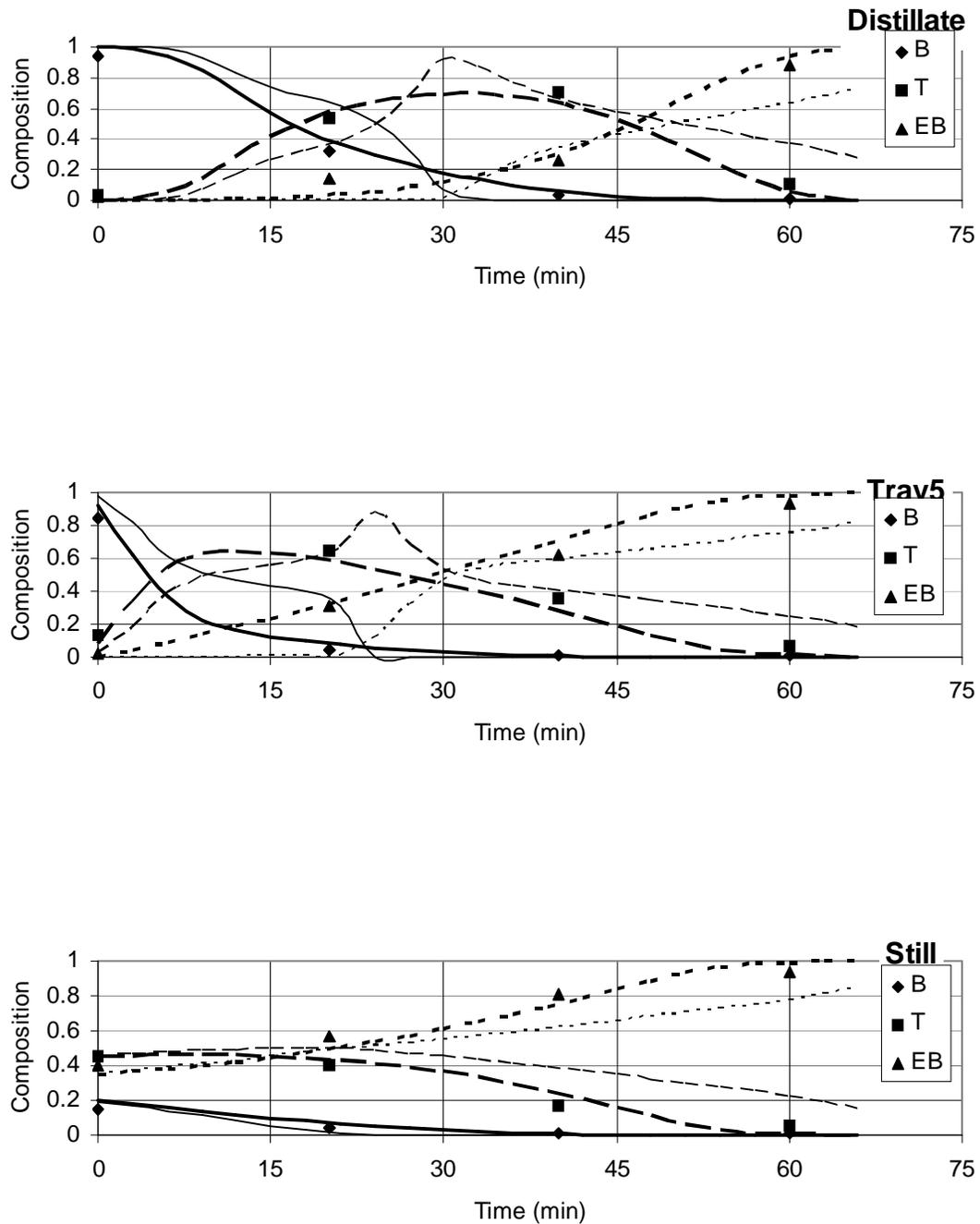
**Figure (6): Experimental and Simulation Results of Equilibrium and Nonequilibrium
Models Experiment no-1 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)**

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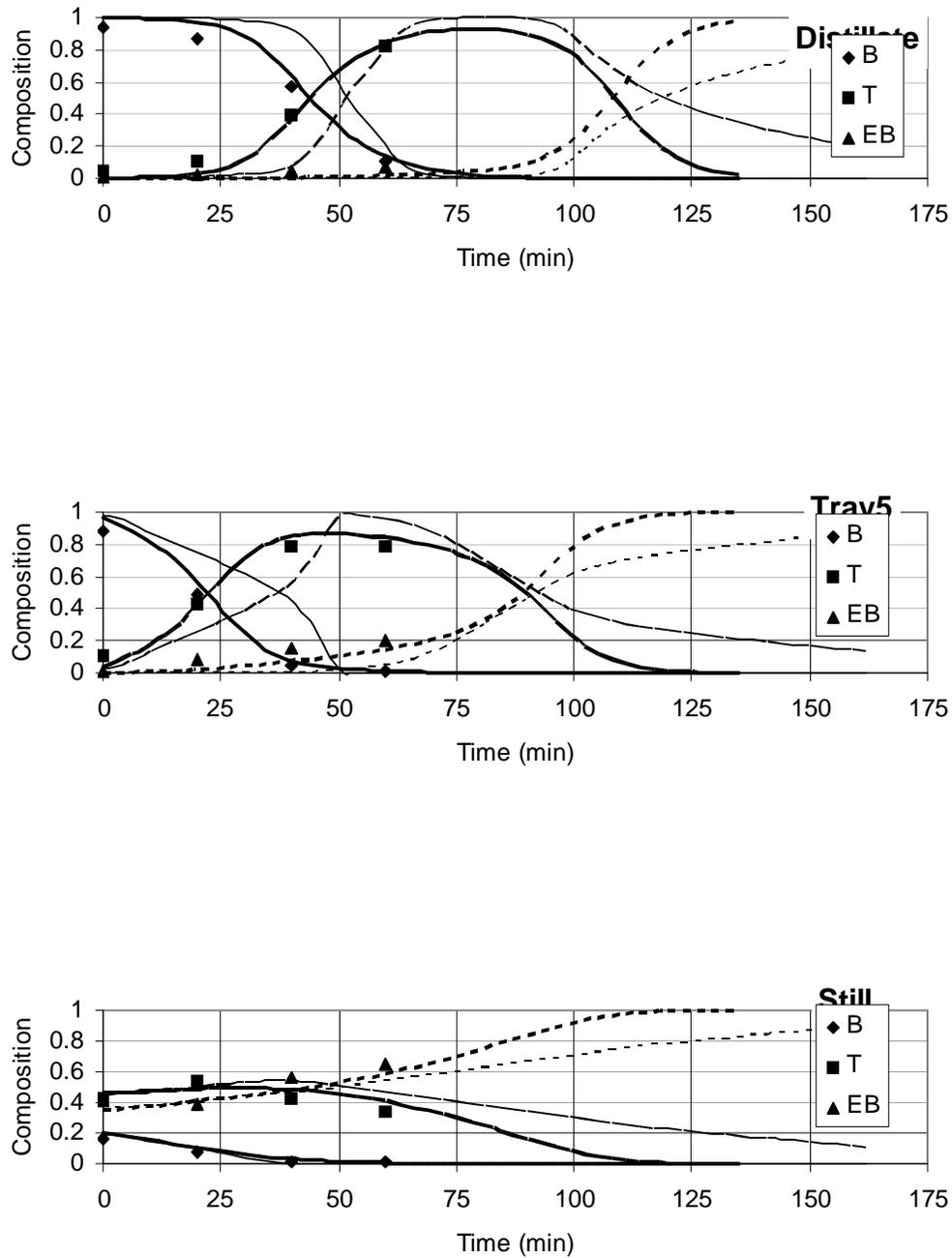
Distillate

Tray5

Still

Figure (7): Experimental and Simulation Results of Equilibrium and Nonequilibrium Models Experiment no-2 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)

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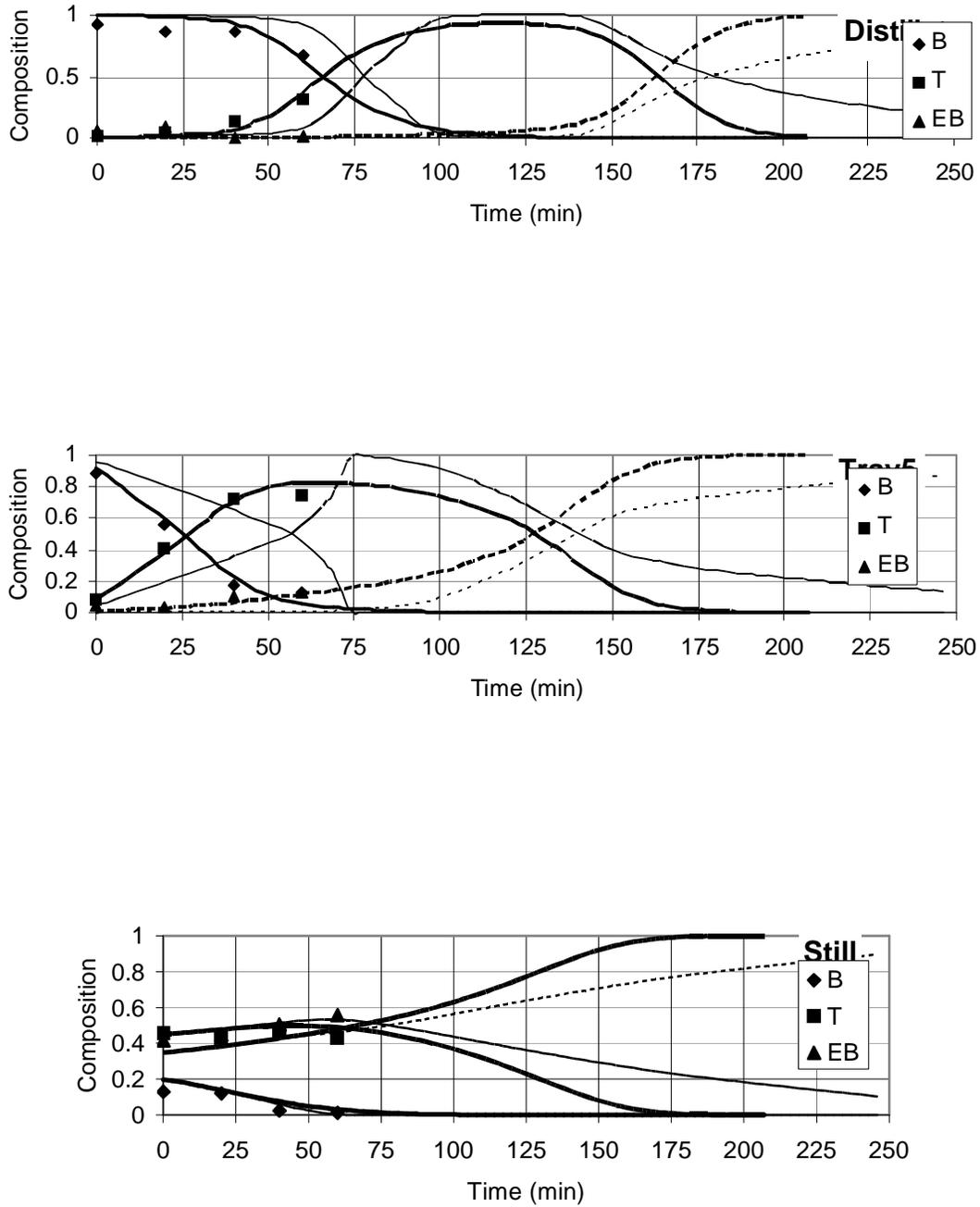Rate-Based Model for Simulation of Batch
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**Figure (8): Experimental and Simulation Results of Equilibrium and Nonequilibrium
Models Experiment no-3 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)**

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Comparison between Equilibrium Model and
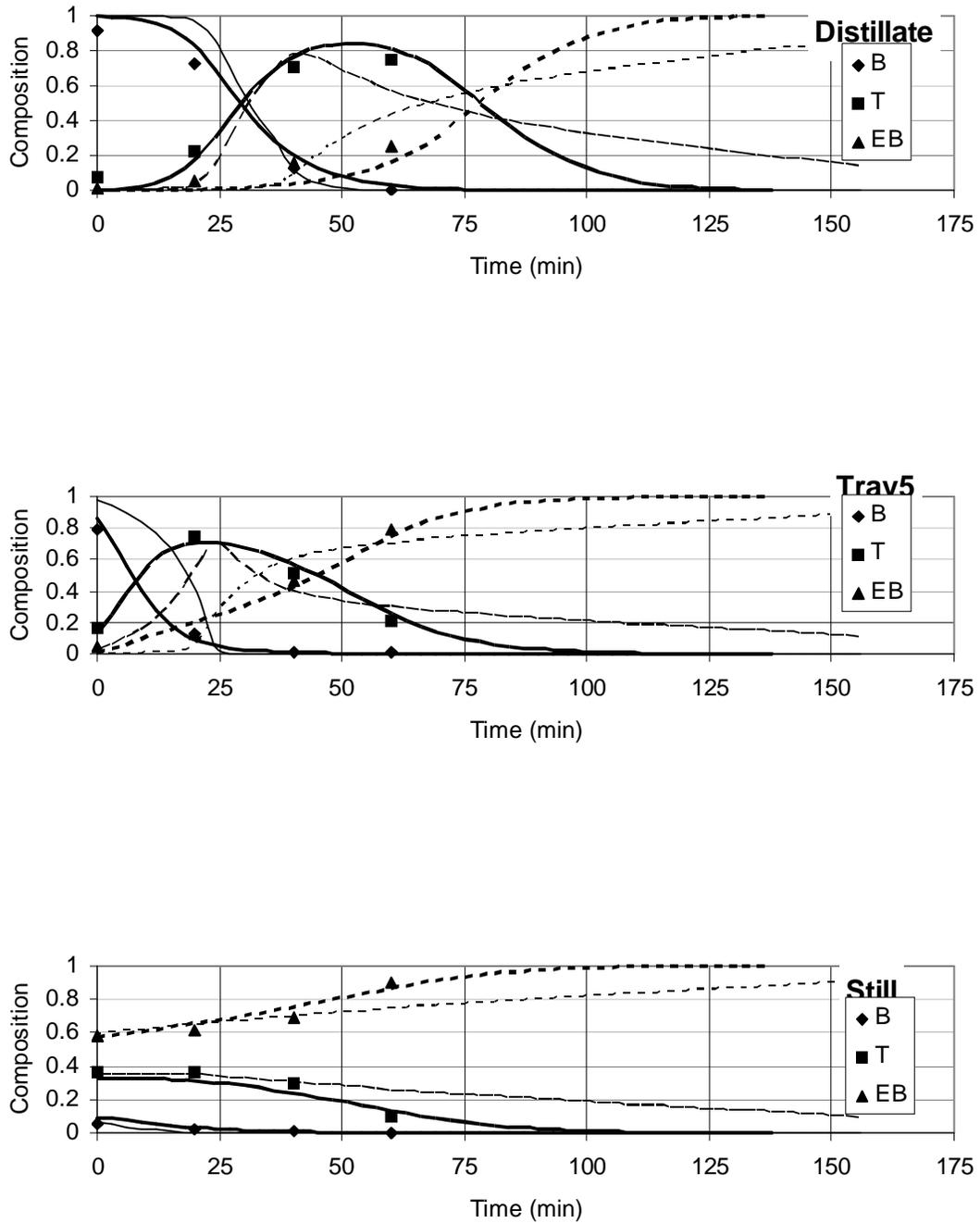Rate-Based Model for Simulation of Batch
Zeotropic Distillation

**Figure (9): Experimental and Simulation Results of Equilibrium and Nonequilibrium
Models Experiment no-4 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)**

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Comparison between Equilibrium Model and
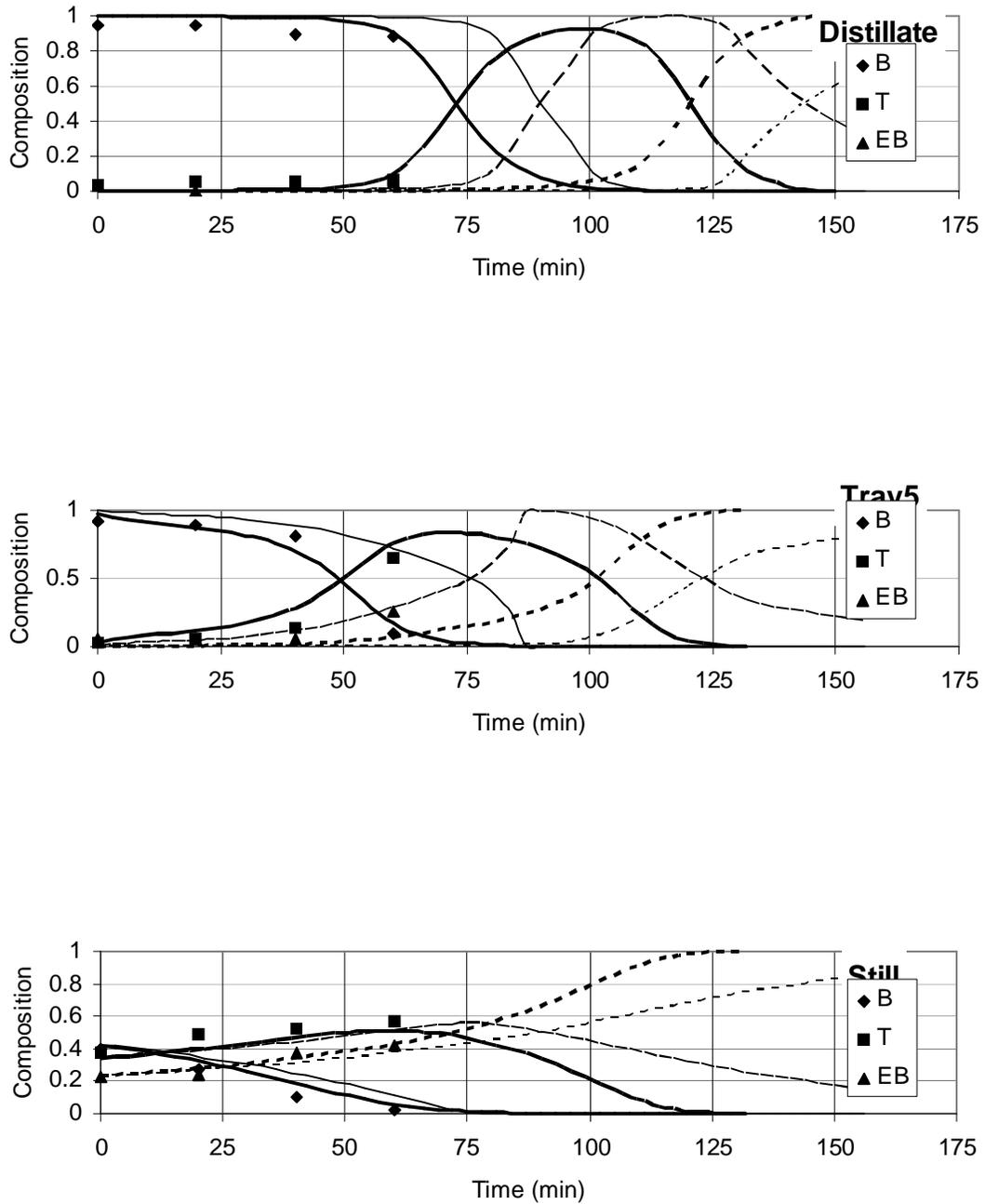Rate-Based Model for Simulation of Batch
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**Figure (10): Experimental and Simulation Results of Equilibrium and Nonequilibrium
Models Experiment no-5 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)**

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Figure (11): Experimental and Simulation Results of Equilibrium and Nonequilibrium Models Experiment no-6 Table (3).
(Points ≡ Exp., Soft lines ≡ EQ model, and Bold Lines ≡ NEQ model)