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Batch Distillation Studies of Some Binary Systems With Liquid Phase Non-Ideality

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Abstract: Simulation studies of batch distillation of some non-ideal binary systems have been carried out and reported in this work. Differential distillation as well as batch distillation at total reflux has been simulated through a semi-rigorous unsteady state mathematical model, implemented via codes developed in-house. The Wilson model has been used to represent non-ideality in the liquid phase and predict-vapour-liquid equilibrium (VLE) data. Parametric studies of the composition and temperature profiles have been carried out. Heating and cooling requirements for batch distillation operation have also been estimated. The model presented here can be used for simulating the start-up of any distillation column for even multi-component non-ideal systems, as long as the VLE data are available for them, without requiring any commercial simulation software. The model can also be extended to simulation of batch distillation columns with a finite value of reflux ratio after suitable modification of the governing equations. Thus it can be used for preliminary design work as well.

Keywords: Batch distillation, Non-ideality, Wilson equation.

I. Introduction

Distillation is a separation process of immense importance to the chemical process industries. The most common form of utilization of this unit operation in industries is continuous distillation in tray or packed columns. A different form viz. batch distillation has found widespread application in the specialty chemical industries such as pharmaceuticals, flavours and fragrance synthesis units, bio-chemical processing etc where a wide variety but low volumes of mixed streams have to be handled. Having separate dedicated continuous columns for several kinds of feed streams will be an expensive proposition in these industries. Batch processing proves to be a more economical mode of operation in these cases [1-5]. This is an inherently dynamic mode of operation, thus the design and analysis of these systems are more complex than those of continuous separation systems. The difficulty is compounded when systems with non-ideal vapour liquid equilibrium characteristics are required to be processed in batch distillation systems. Most well known shortcut method of column design fail to provide useful insights into the design of columns for such separation duties. Other methods reported in literature are either too complicated to be of practical use to designers [5] or too system-specific [6] and hence difficult or impossible to apply to any general mixture.

In this work batch distillation of three binary systems is considered where there is significant liquid phase non-ideality (marked by the formation of homogeneous binary azeotropes in each case). The systems have been so chosen that they exhibit formation of maximum boiling azeotrope, minimum boiling azeotrope and tangent pinch respectively. The vapour liquid equilibrium is represented by modified form of Raoult's law and activity coefficient data have been calculated using Wilson's two-parameter activity coefficient model. Two modes of batch distillation viz. differential distillation without reflux and batch distillation with a column section and under total reflux conditions have been studied. Semi-rigorous mathematical models have been developed for determination of the dynamic composition profiles under different conditions and implemented through codes developed in-house. These help model the start up of any distillation column and they can be extended to operation of batch columns with distillate product or reboiler product withdrawal too. They can also be used for parametric studies and to obtain some preliminary design data for columns such as minimum number of trays or maximum separation possible for given number of trays. It is the aim of this work to provide a simple way for batch distillation column performance evaluation, particularly obtaining the dynamic composition profiles and time for attaining steady state under total reflux conditions for non-ideal systems without depending on commercial process simulator software.

II. Thermodynamic Data and Model Equations

A. Thermodynamic Data

The completely miscible, non-ideal binary systems considered in this work are the following:

- Methanol-toluene

- Acetone-chloroform
- Chloroform-methanol

For predicting the vapour-liquid equilibrium behaviour of these systems, pure component vapour pressure data for each species are obtained from Antoine equation [8]:

$$\log_{10} P^{sat} = A - \frac{B}{T+C} \tag{1}$$

The two-parameter Wilson equation [9-11] is used to model the liquid phase binary interaction and non-ideality for all the systems. Parameters for this model for each system are obtained from literature [9-11] and are presented in Tables I, II and III respectively. This model is chosen for the computational ease and accuracy that it offers. The expressions for the activity coefficients in the binary system according to this model are

$$ln\gamma_1 = -\ln\left(x_1 + E_{AB}x_2\right) + x_2\left[\frac{E_{AB}}{x_1 + E_{AB}x_2} - \frac{E_{BA}}{E_{BA}x_1 + x_2}\right] \tag{2}$$

$$ln\gamma_2 = -\ln\left(x_2 + E_{BA}x_1\right) - x_1\left[\frac{E_{AB}}{x_1 + E_{AB}x_2} - \frac{E_{BA}}{E_{BA}x_1 + x_2}\right] \tag{3}$$

where the terms E_{AB} and E_{BA} are given by

$$E_{AB} = \frac{v_2}{v_1}\exp\left[-\frac{a_{12}}{RT}\right] \tag{4}$$

$$E_{BA} = \frac{v_1}{v_2}\exp\left[-\frac{a_{21}}{RT}\right] \tag{5}$$

TABLE I: THERMODYNAMIC DATA FOR SYSTEM 1

	Methanol (CH_3OH)			*Toluene* ($C_6H_5CH_3$)		
Antoine equation coefficients	A=8.08097	B=1582.271	C=239.726	A=6.95087	B=1342.31	C=219.187
Molar volume (cm^3/gmol)	40.73			106.3		
Wilson equation parameters (J/mol)	a12=7677.1579, a21=1097.106					
Latent heat of vapourization (kJ/mol)	35.21			33.18		
Specific heat capacity (J/mol K)	81.08			157.0		

TABLE II: THERMODYNAMIC DATA FOR SYSTEM 2

	Acetone (CH_3COCH_3)			*Chloroform* ($CHCl_3$)		
Antoine equation coefficients	A=7.11714	B=1210.595	C=229.664	A=6.95465	B=1170.966	C=226.232
Molar volume (cm^3/gmol)	74.03			80.48		
Wilson equation parameters (J/mol)	a12=839.0968, a21=-2612.2876					
Latent heat of vapourization (kJ/mol)	31.3			31.4		
Specific heat capacity (J/mol K)	125.5			114.25		

TABLE III: THERMODYNAMIC DATA FOR SYSTEM 3

	Chloroform ($CHCl_3$)			*Methanol* (CH_3OH)		
Antoine equation coefficients	A=6.95465	B=1170.966	C=226.232	A=8.08097	B=1582.271	C=239.726
Molar volume (cm^3/gmol)	80.48			40.73		
Wilson equation parameters(J/mol)	a12=-1513.4945, a21=7086.611					
Latent heat of vapourization (kJ/mol)	31.4			35.21		
Specific heat capacity (J/mol K)	114.25			81.08		

B. Differential Distillation

Schematic diagram of the system for differential distillation is shown below. A charge of liquid of known composition is first placed in the still and heat is provided. The vapour rising from the boiling liquid in the still is totally condensed and collected in a separate vessel and this leads to change of liquid composition progressively with time. There is no material return stream (i.e. reflux) to the still and the liquid hold up in the still continues to decrease with time as distillate is collected from the top. The entire process takes place at constant pressure.

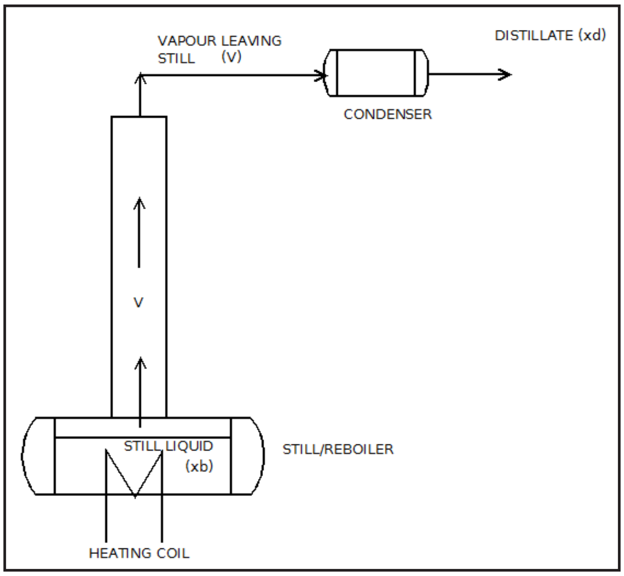


Fig. 1: Set-Up for Differential Distillation

The material balance equation and equilibrium relation for differential distillation is expressed as [9, 12, 13]:

$$ln\frac{W}{W_o} = \int_{x_{o1}}^{x_{f1}} \frac{dx}{y_1 - x_1} \tag{6}$$

$$y_1 P_T = \gamma_1 x_1 P_1^{sat} \tag{7}$$

The approximate amount of heat input needed to maintain a constant boil up rate depends on the composition and temperature of the residual liquid in the still or reboiler at any instant of time. Assuming no heat losses from the still and constant values of specific heats and latent heats of vapourization of all components over the temperature range of interest, it can be expressed as follows:

$$Q_{in} = V(x_{b1}C_{p1}\left(T_{still} - T_{ref}\right) + x_{b1}\lambda_1 + x_{b2}C_{P2}\left(T_{still} - T_{ref}\right)$$

$$+x_{b2}\lambda_2) - \overline{C_p}TV + W\overline{C_p}\frac{\Delta T_{still}}{\Delta t} \tag{8}$$

Still temperature at any time was determined through an iterative bubble point calculation from known liquid composition and pressure.

C. Batch Distillation With Total Reflux

Schematic diagram of the system for batch distillation with total reflux is shown below. A charge of liquid of known composition is first placed in the still and heat is provided. The vapour rising from the boiling liquid in the still is totally condensed and returned back in the form of total reflux to the column which has either a certain number of trays or a certain height of packing material provided for good vapour-liquid contact and efficient mass transfer. A concentration profile gradually evolves in the reboiler, column section and the reflux condenser with time and a steady state is reached at one point of time depending on the system dynamics, particularly hold ups in the different sections of the system.

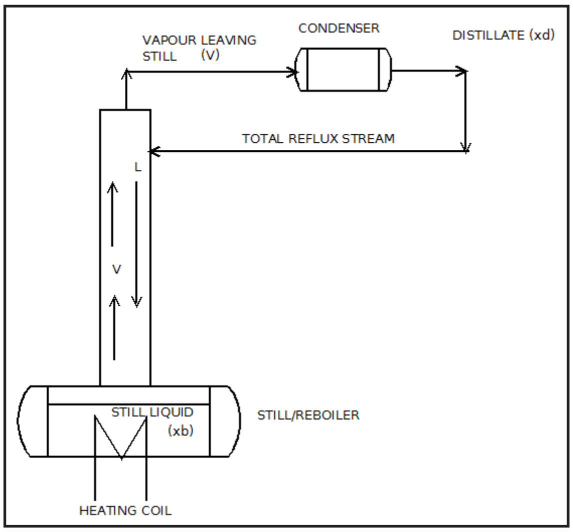


Fig. 2: Set-Up for Batch Distillation at Total Reflux

For the reboiler, trays and overhead condenser of the batch distillation column at total reflux, the material balance equations for species j can respectively be written as:

For the reboiler or still (tray number N+1):

$$M_B\frac{dx_{N+1,j}}{dt} = Lx_{N,j} - Vy_{N+1,j} \tag{9}$$

For the trayed section (for tray number n where n varies from 2 to N):

$$M_t\frac{dx_{n,j}}{dt} = L(x_{n+1,j} - x_{n,j}) - V(y_{n-1,j} - y_{n,j}) \tag{10}$$

For the reflux drum (tray number 1):

$$M_D\frac{dx_{1,j}}{dt} = Vy_{2,j} - Lx_{1,j} \tag{11}$$

For operation under total reflux condition, V is equal to L. The vapour-liquid equilibrium relationship for the multi-component non-ideal system is expressed as:

$$y_{i,j} = \frac{\gamma_j x_{i,j} P_j^{sat}}{\sum \gamma_j x_{i,j} P_j^{sat}} \tag{12}$$

Tray temperatures were determined iteratively from known liquid composition and tray pressure.

The model assumptions are as follows [14]:

(a) The vapour phase is taken as ideal on account of relatively low pressure (about 760 Torr) condition of distillation while the liquid phase is non-ideal.

(b) The stages in batch distillation column are assumed to be 100% efficient and the liquid and the vapour streams leaving each tray are in equilibrium.

(c) The liquid volume or hold up in the reboiler, reflux drum and on the hypothetical column plates are well-mixed regions having uniform composition, so no spatial variation of composition in the radial direction are envisaged. The liquid leaving each tray has been taken to have the same composition as that of the liquid on the tray.

(d) The dynamics of the overhead pipe work and condenser are negligible; hence there are no time lag elements in the system. The dynamics of the vapour phase in the column are much faster than that of the liquid phase and are neglected.

(e) The liquid hold-ups are constant on each tray and in the reboiler and reflux drums. Vapour hold ups are not considered in the model equations.

(f) The column has been considered to have no heat losses through the walls, hence enthalpy balances are not considered in this study, except for reflux condenser and reboiler heat duty calculations. From the very similar values of latent heat of vapourization of the species in each binary mixture it can also be established that the assumption of constant molar overflow will also be valid for these systems.

(g) A constant operating pressure has been assumed for generating the VLE data and for the simulation studies.

The material balance equations and equilibrium relationship were written for each component on each tray and simultaneously integrated using standard techniques for numerical solution of ordinary differential equations to obtain the time dependent composition profiles of each species on each tray. The entire set of model equations represents a differential-algebraic equation system. For each tray, bubble point calculations were performed first for tray temperature determination and activity coefficient values were calculated at the determined bubble point. Calculations were continued using the ‘time marching’ method till steady state compositions were attained on each tray. For total reflux operation, a given quantity of the feed was assumed to be fed to the sump. The initial feed composition as well as the initial composition of the liquid on each tray and reflux drum were specified. The numerical integration was carried out with the assumed initial composition profile. The values of the hold up in the sump and on each tray were taken as constants for a particular run. The vapour boil up rate can be varied by varying the heat input (steam flow rate or electrical heater power output) to the sump liquid and it is assumed that the required vapour flow rate is instantly established by neglecting heat transfer dynamics in the reboiler. The evolution of the composition profiles on each tray of the tower was then determined and the compositions at steady state were obtained.

III. Results and Discussion

A. Differential Distillation

The vapour liquid equilibrium diagrams were first generated for each of the three systems at a total pressure of 1 atm (a). Starting with a chosen value of the initial still liquid composition, the progressive change in the composition of the condensate at the top of the still was obtained by integration of Eqn. 1. The still temperatures were evaluated by a bubble point calculation at each time from the residual liquid temperature and constant total pressure. The boil up was assumed to be maintained constant at 10 mol/hr in every case.

i. System 1

The T-x-y diagram (Fig. 3) shows the presence of the tangent pinch and formation of minimum boiling azeotrope in this system. Fig. 4 shows that when distilling an initially 50% mixture of methanol in toluene (i.e. composition leaner than the azeotropic composition), the still liquid continues to get leaner in lower boiling methanol but the average distillate composition does not vary much and remains leaner than the azeotropic composition. Towards the end of the process when practically only toluene is left, there is sharp rise in still temperature to the boiling point of pure toluene.

When distilling a mixture that is initially richer in methanol than the azeotropic composition (Fig. 5), the distillate is initially poorer in methanol than the still liquid despite being the lighter component and ultimately the still liquid and vapour leaving it acquires the same (i.e. azeotrope) composition. Temperature practically remains constant during distillation with a sharp rise only at the end.

ii. System 2

Formation of a maximum boiling azeotrope is indicated in Fig. 6 for system 2. When initial content of the lower boiling species is leaner than azeotropic composition (Fig. 7), then the still composition remains leaner than a zeotrope at all times and distillate remains leaner than still liquid in the lower boiling species. When initial content of the lower boiling species is richer than azeotropic composition (Fig. 8), the reverse happens till the azeotropic composition is attained after which there is no further separation possible.

iii. System 3

Formation of a minimum boiling azeotrope is indicated in Fig. 9 for system 2. When initial content of the lower boiling species is leaner than azeotropic composition (Fig. 10), then the still composition remains leaner than azeotrope at all times and distillate remains richer than still liquid in the lower boiling species. When initial content of the lower boiling species is richer than azeotropic composition (Fig. 11), the reverse happens till the azeotropic composition is attained after which there is no further separation possible.

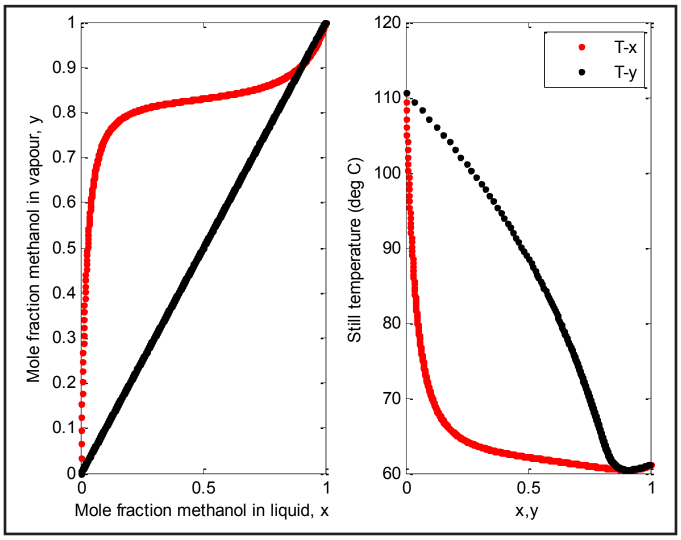


Fig. 3: Calculated x-y and T-x-y Diagram of System 1 at 1 atm Pressure

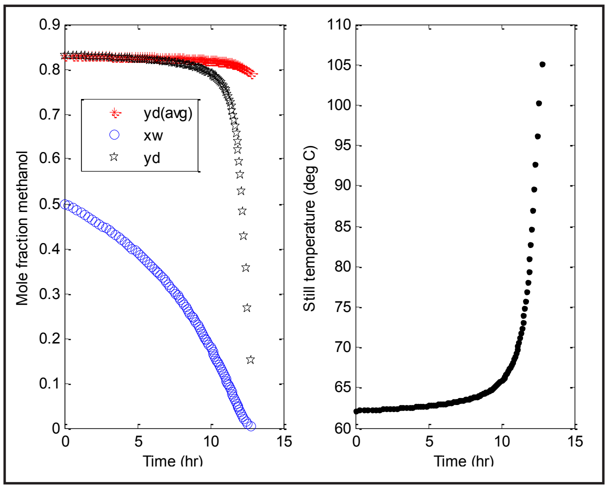


Fig. 4: Still Temperature and Composition Profiles for Differential Distillation of System 1 with $x_o = 0.5$

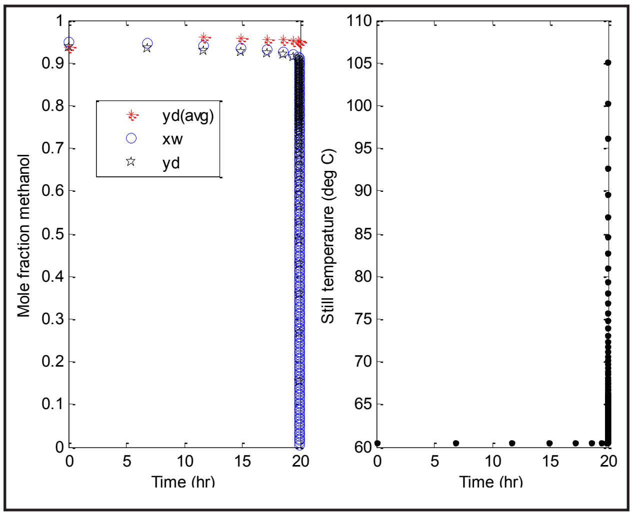


Fig. 5: Still Temperature and Composition Profiles for Differential Distillation of System 1 with $x_o = 0.95$

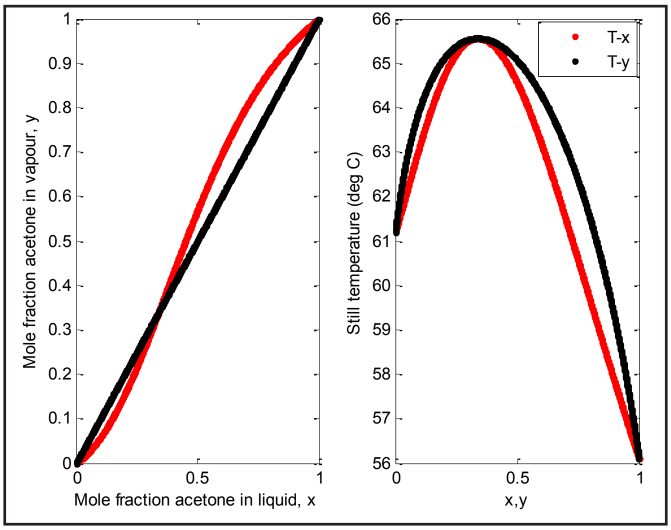


Fig. 6: Calculated x-y and T-x-y Diagram of System 2 at 1 atm Pressure

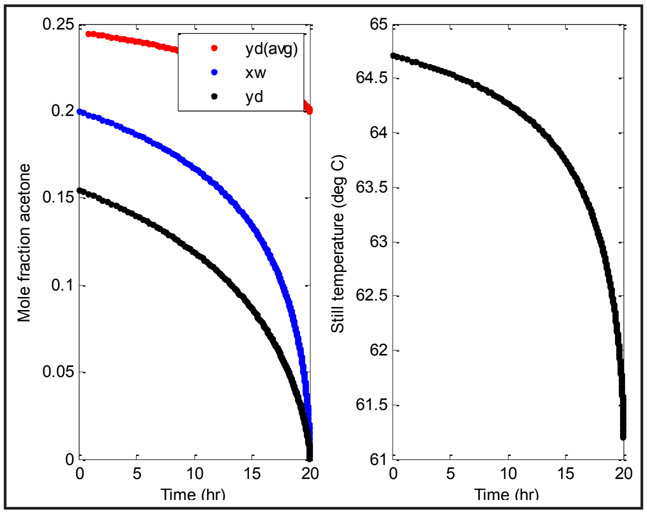


Fig. 7: Still Temperature and Composition Profiles for Differential Distillation of System 2 with $x_o = 0.2$

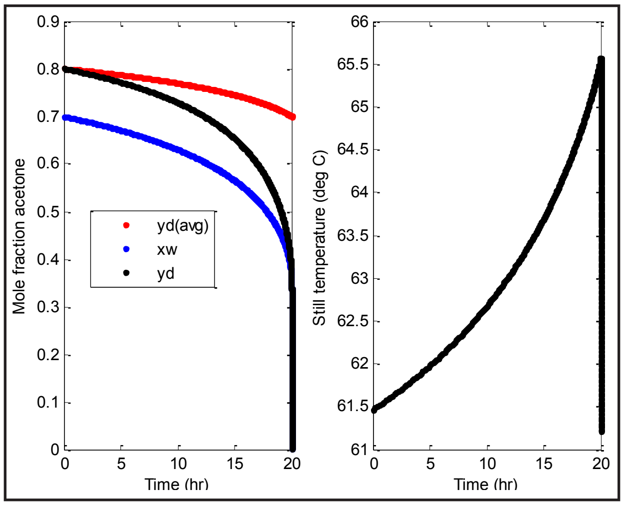


Fig. 8: Still Temperature and Composition Profiles for Differential Distillation of System 2 with $x_o = 0.7$

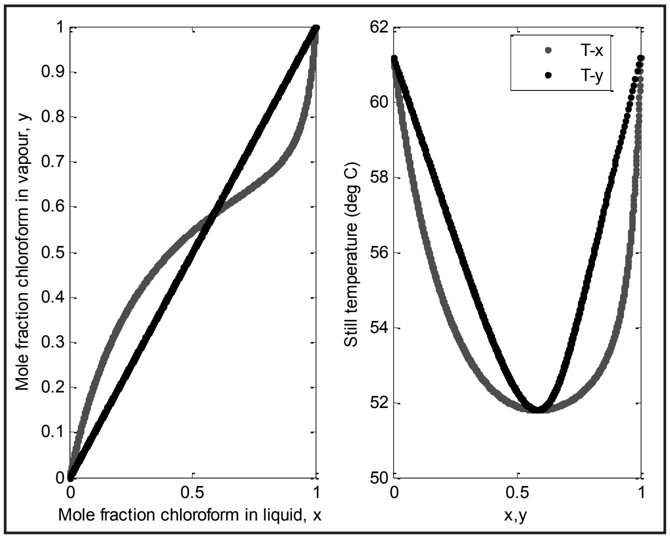


Fig. 9: Calculated x-y and T-x-y Diagram of System 3 at 1 atm Pressure

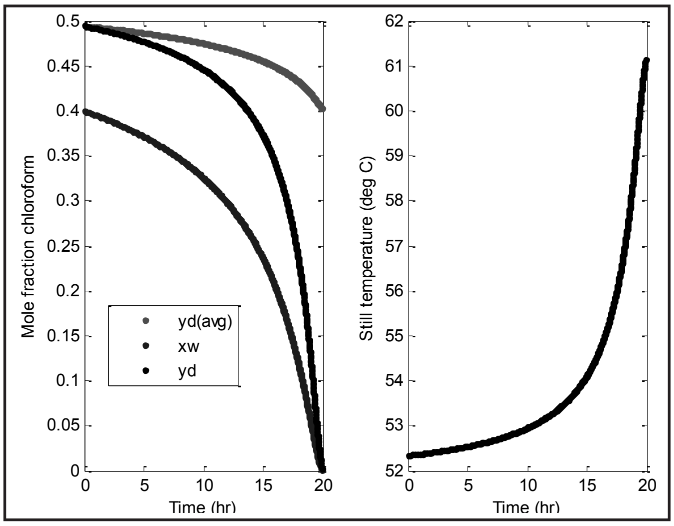


Fig. 10: Still Temperature and Composition Profiles for Differential Distillation of System 3 with $x_o = 0.4$

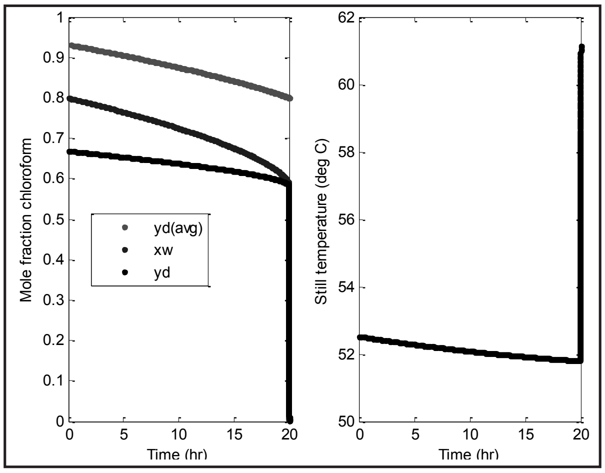


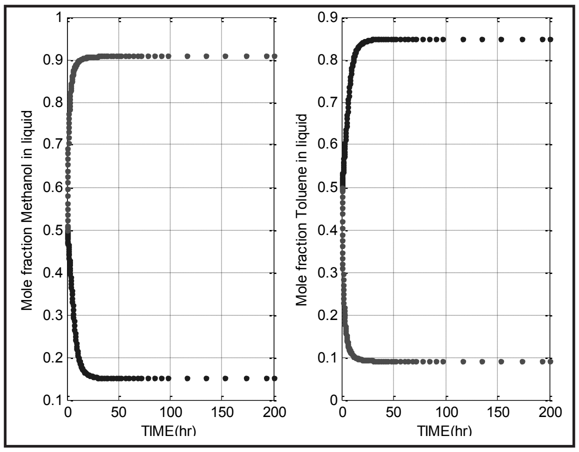
Fig. 11: Still Temperature and Composition Profiles for Differential Distillation of System 3 with $x_o = 0.8$

B. Batch Distillation at Total Reflux

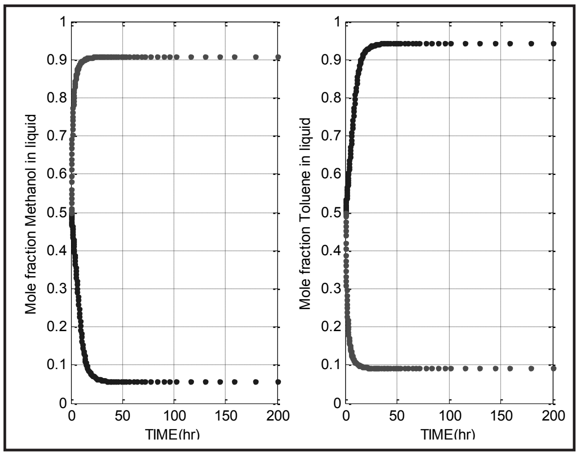
For each binary system, evolution of dynamic composition profiles in the reflux drum and the bottom still or reboiler are presented in Fig. 12-Fig. 17 below. For each system, in one case the initial feed liquid composition was varied while keeping number of ideal trays constant in the column section (10 trays excluding the reboiler and condenser) and in the other case, the number of trays was varied (from 15 to 20) while keeping starting liquid composition fixed. The boil up was maintained constant at 10 mol/hr in every case.

i. System 1

From Fig. 12 it is observed that the azeotropic composition is achieved at the reflux condenser and there is no improvement in the top condenser composition beyond the azeotropic point even with change in number of trays in the column section at total reflux. Thus the simulation code correctly predicts the location and formation of the azeotrope in the binary system. Fig. 13 shows that the location of formation of the azeotropic mixture changes from condenser to still when initial feed mixture changes from leaner that azeotrope to richer than azeotrope, with respect to the low boiling species.

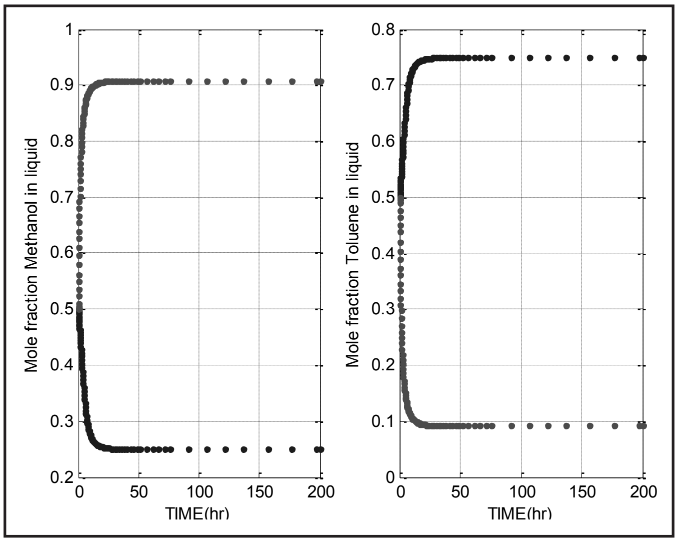


(a) N = 15 (Black: Still, Grey: Condenser)

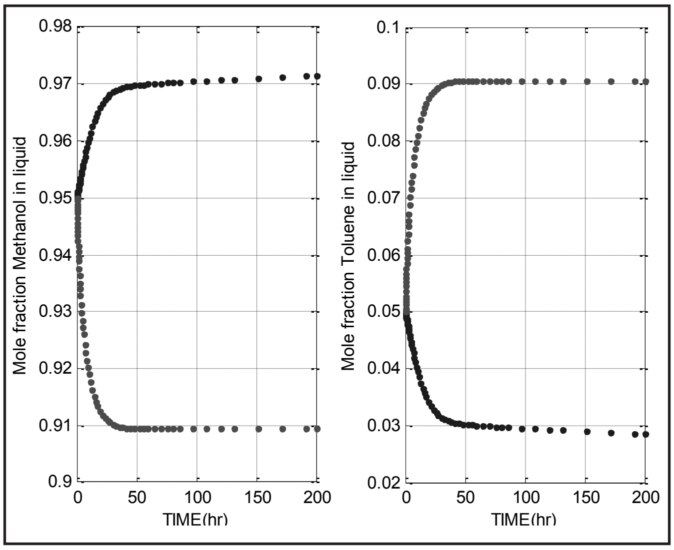


(b) N = 20 (Black: Still, Grey: Condenser)

Fig. 12 (a) & (b): Dynamic Composition Profiles in Batch Distillation for $x_o = 0.5$ for System 1 and Differing Number of Trays in the Column Section



(a) x_0 = 0.5 (Black: Still, Grey: Condenser)



(b) x_o = 0.95 (Black: Still, Grey: Condenser)

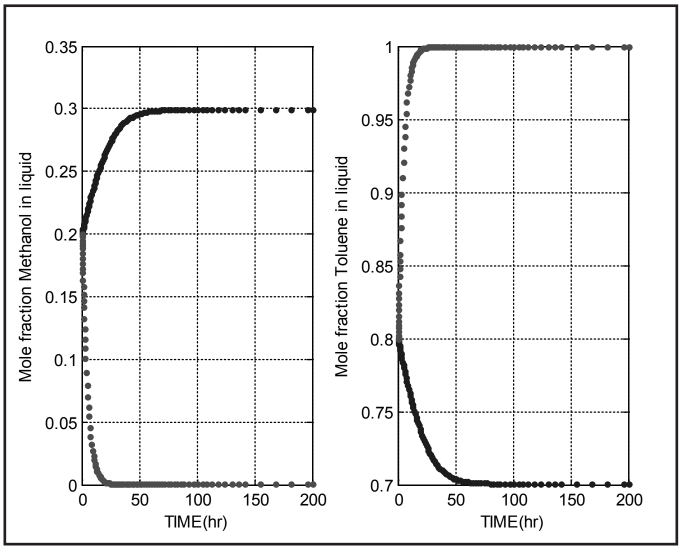
Fig. 13 (a) & (b): Dynamic Composition Profiles in Batch Distillation for N = 10 for System 1 and Differing Initial Still Liquid Composition

ii. System 2

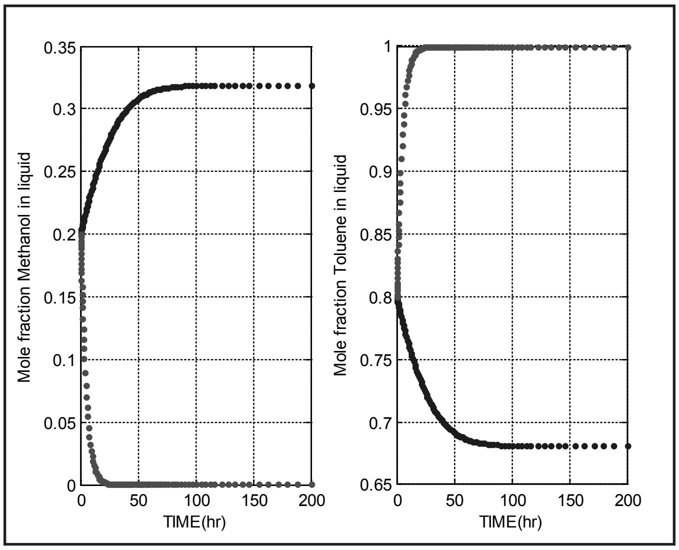
From Fig. 14 it is observed that the azeotropic composition is achieved at the still and there is no further improvement in the still composition beyond the azeotropic point even with change in number of trays in the column section at total reflux. Thus the simulation code correctly predicts the location and formation of the azeotrope in the binary system. Fig. 15 shows that the location of formation of the azeotropic mixture changes from still to top condenser when initial feed mixture changes from leaner that azeotrope to richer than azeotrope, with respect to the low boiling species.

iii. System 3

From Fig. 16 it is observed that the azeotropic composition is achieved at the reflux condenser and there is no improvement in the top condenser composition beyond the azeotropic point even with change in number of trays in the column section at total reflux. Thus the simulation code correctly predicts the location and formation of the azeotrope in the binary system. Fig. 17 shows that the location of formation of the azeotropic mixture changes from condenser to still when initial feed mixture changes from leaner that azeotrope to richer than azeotrope, with respect to the low boiling species.

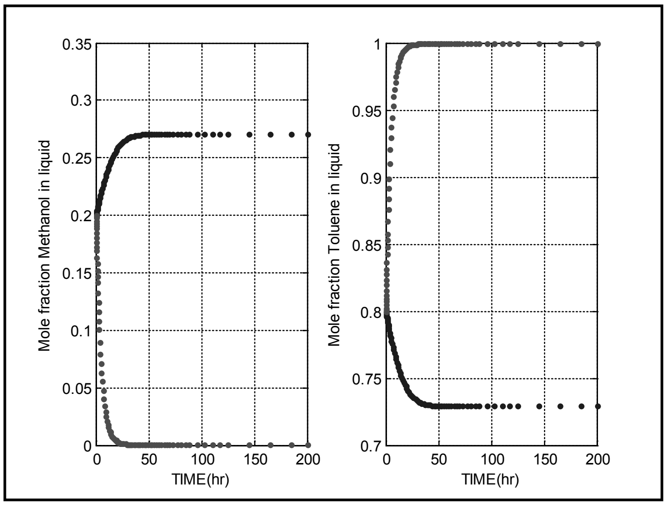


(a) N = 15 (Black: Still, Grey: Condenser)

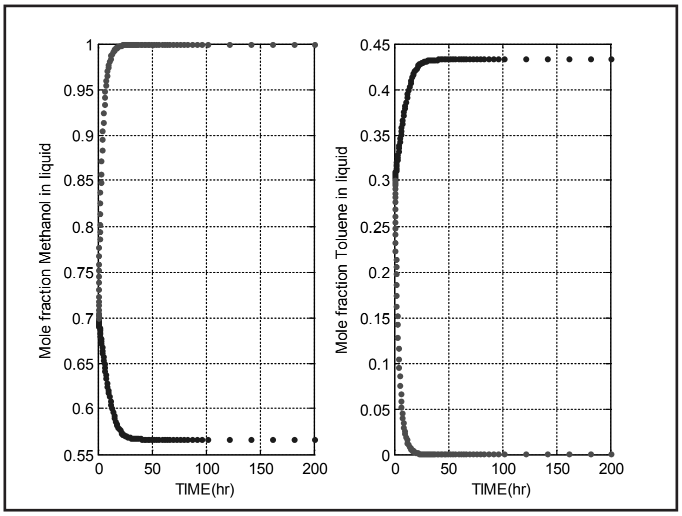


(b) N = 20 (Black: Still, Grey: Condenser)

Fig. 14 (a) & (b): Dynamic Composition Profiles in Batch Distillation for x_0 = 0.2 for System 2 and Differing Number of Trays

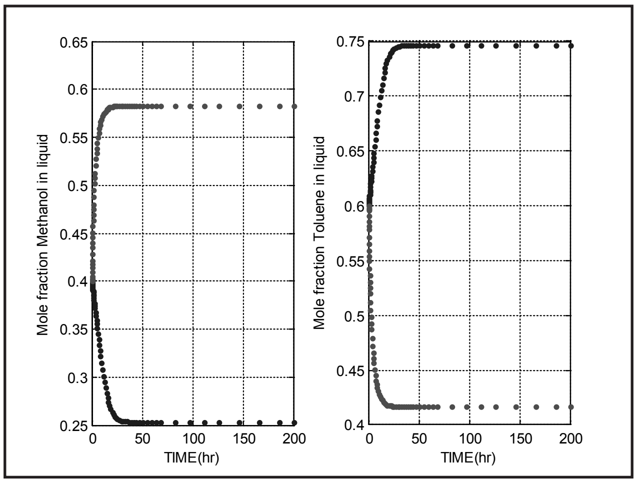


(a) $x_0 = 0.2$ (Black: Still, Grey: Condenser)

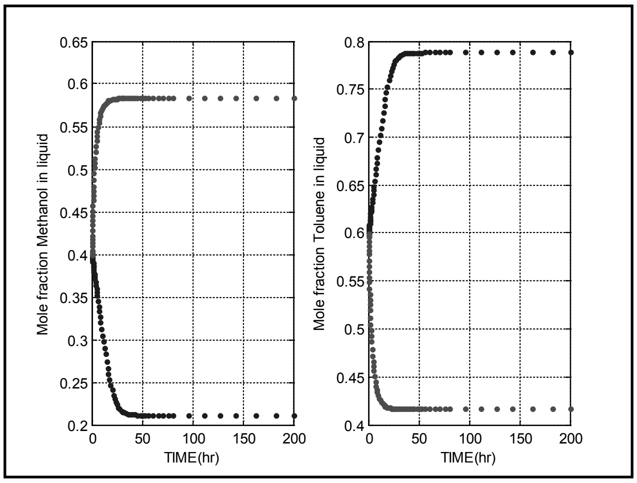


(b) $x_0 = 0.7$ (Black: Still, Grey: Condenser)

Fig. 15 (a) & (b): Dynamic Composition Profiles in Batch Distillation for N = 10 for System 2 and Differing Initial Still Liquid Composition

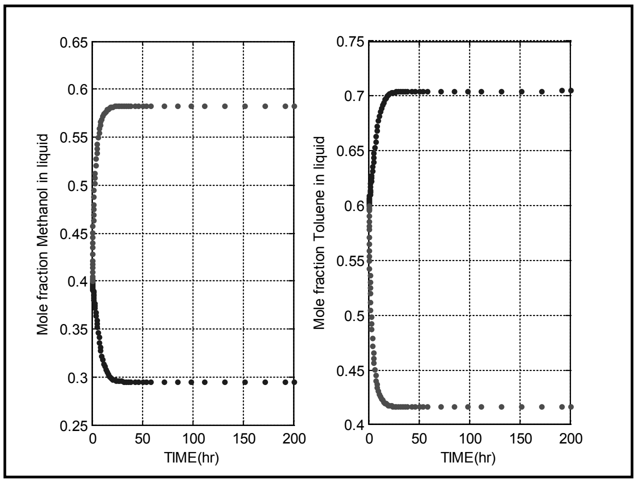


(a) N = 15 (Black: Still, Grey: Condenser)

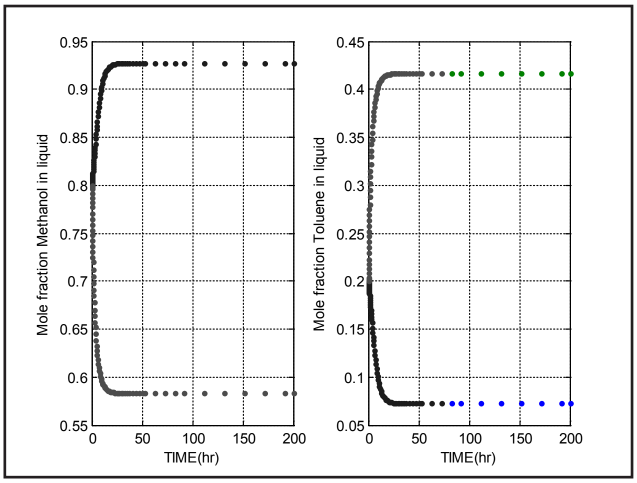


(b) N = 20 (Black: Still, Grey: Condenser)

Fig. 16 (a) & (b): Dynamic Composition Profiles in Batch Distillation for $x_0 = 0.4$ for System 3 and Differing Number of Trays



(a) $x_o = 0.4$ (Black: Still, Grey: Condenser)



(b) $x_o = 0.8$ (Black: Still, Grey: Condenser)

Fig. 17 (a) & (b): Dynamic Composition Profiles in Batch Distillation for N = 10 for System 3 and Differing Initial Still Liquid Composition

An example of the dynamic tray to tray composition calculations till attainment of steady state is shown in Fig. 18 for System 1 with a 50-50 feed mixture. The time for attaining steady state is strongly influenced by the values of liquid hold up in the still, condenser and the trays. The emphasis in this work was on developing the codes to predict the evolution of the steady profiles in batch distillation under total reflux and not the precise time for column equilibration. Thus the values of hold ups were selected randomly, without considering precise hydrodynamics of the column or its components. Actual tray or packed column hydraulics can also be included in this model to obtain more accurate representations of the liquid phase hold ups.

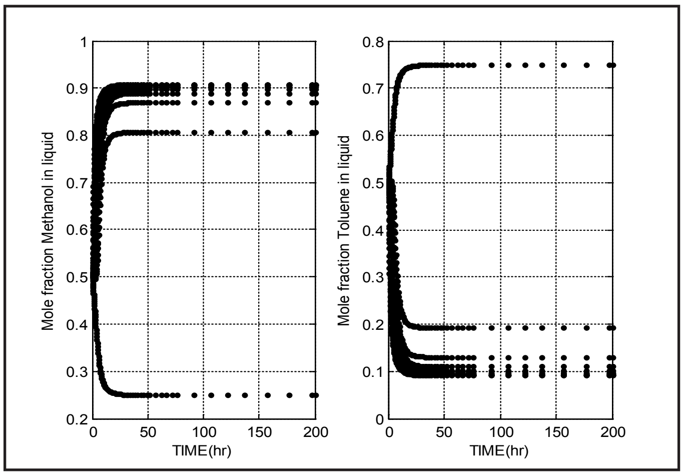


Fig. 18: Tray to Tray Dynamic Composition Profiles in Batch Distillation for N = 10 for System 1 ($x_o = 0.5$)

IV. Summary and Conclusion

Batch distillation is one of those special unit operations which are very important for industries processing low volumes of a diverse range of high value products, such as the pharmaceutical industries, fine chemicals industries etc. Mathematical model and simulation codes for studying the dynamic behaviour of a batch still for differential distillation and batch column distillation under total reflux operation have been developed and used in this work to study three well known non-ideal binary systems. The semi-rigorous method can be extended to ternary or higher order non-ideal mixtures as well provided their VLE data are completely available. There are specific methods available in literature for dealing with binary azeotropic batch distillation [14] but this method is a generalized one applicable for all such systems. The method shown here can be extended to batch columns with finite values of reflux as well. Column hydrodynamic considerations can also be incorporated in this model through suitable equations representing the hydraulic behaviour of the tray or packed column section. The method correctly predicts the nature and composition of azeotropes though this is strongly dependent on the accuracy of the VLE equation parameters. It also correctly predicts the location where the azeotrope forms depending on the starting composition of the feed mixture. This establishes its usefulness for making parametric studies and preliminary design work without the need for special software or an extensive set of inputs for initiating the calculations.

Nomenclature

a_{12}, a_{21}	Binary interaction parameters in Wilson activity coefficient model, J/mol
A	Antoine equation coefficient for any species, dimensionless
B	Antoine equation coefficient for any species, $^oC^{-1}$
C	Antoine equation coefficient for any species, ^oC
C_p	Molar specific heat of any pure species, J/mol K
$\overline{C_p}$	Average molar specific heat of a mixture, J/mol K
E_{AB}, E_{BA}	Binary interaction parameters in Wilson activity coef.ficient model, dimensionless
i	Species number index, dimensionless
L	Liquid flow rate in total reflux condition, mol/h
M_b	Liquid hold up in still/reboiler at any time, mol
M_d	Liquid hold up in reflux drum at any time, mol
M_t	Liquid hold up on each tray at any time, mol
N	Number of trays in column section, dimensionless
P^{sat}	Saturation vapour pressure of a pure species, Torr
P_T	Total system pressure, Torr
Q_{in}	Heat input to reboiler/still in batch distillation, W
T	Temperature, ^oC
$T_{reference}$	Reference temperature for enthalpy calculations, ^oC
T_{still}	Reboiler/still temperature in batch distillation, ^oC
v_1, v_2	Molar volumes of pure species 1 and 2 respectively, cm^3/mol
V	Constant vapour boil up rate, mol/h
W_o	Initial moles of liquid feed to the still/reboiler, mol
W	Moles of liquid left in the still/reboiler at any time, mol
x_o	Mole fraction of more volatile species in the initial liquid fed to the reboiler/still, dimensionless
x_{b1}, x_{b2}	Mole fraction of more volatile and less volatile species in the still liquid at any time, dimensionless
x_d	Distillate mole fraction of more volatile species (after complete condensation), dimensionless
y_1	Vapour mole fraction of more volatile species in equilibrium with still liquid at any time, dimensionless

γ_1, γ_2	Activity coefficient of species 1 and 2 respectively at given composition, dimensionless
Δt	Time interval, s
ΔT	Temperature change in still during differential distillation, ^oC
λ_1, λ_2	Molar latent heat of vapourization of pure species 1 and 2, J/mol K

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