

# Numerical Simulation of a Catalytic Distillation Column for Ethyl Acetate Production

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*Abstract:* - This work concentrates on simulation studies of a catalytic distillation for an ethyl acetate production from ethanol and acetic acid. An equilibrium stage model taking into account a kinetically controlled reaction model for liquid phase esterification are used to describe the catalytic distillation column whereas the non-ideality of the vapor and liquid phase equilibrium is described by the activity coefficient model calculated from UNIFAC method. The iterative procedure of a modified bubble-point algorithm is proposed to solve the resulting model equations. It has been found that an initial guess of vapor molar flow rate is the important step affecting whether the solution is converged. By comparing the simulation results obtained from the developed model and Aspen Plus commercial software, it can be seen that the model predictions are in good agreement with the results calculated from Aspen Plus. Since the design and operation of catalytic distillation systems are considerably more complicated than a conventional distillation, the simulations are performed to investigate the influence of various operating parameters on the performance of the catalytic distillation column.

*Key-Words:* - Catalytic Distillation; Steady-State Simulation; Esterification; Ethyl Acetate.

## 1 Introduction

Stronger competition, tougher environmental and safety regulation, and rapidly changing economic condition have an impact on the design of chemical processes for better material and energy utilization and less pollution. Considerable attention from both academic and industrial sectors, therefore, is directed toward the research area of process intensification leading to a substantially smaller and more energy-efficient process [1]. The important example which has been most cited in the recent advanced applications of the process intensification is a multifunctional reactor in which additional functionalities are integrated with a conventional reactor in order to improve the performance of traditional multi-unit processes consisting of a train of reaction and separation processes with recycle streams [2].

A catalytic distillation where chemical reaction and separation are carried out simultaneously in a single distillation column, is one of the widely used multifunctional reactors. It offers several benefits including increased yield due to overcoming chemical equilibrium restrictions, reduced energy consumption by heat integration between the reaction and separation, and improved economics with great potentials for saving equipment and energy costs [3]. As a consequence, a number of the applications of catalytic distillation in chemical and

petroleum industries has been increased rapidly.

In general, the design and operation of catalytic distillation systems are considerably more complex than those involved in either conventional reactors or conventional distillations. Nonlinear phenomena, which are caused by interactions of reaction kinetics, phase equilibrium and mass transfer and strong influences of various operating parameters, leads to the complicated behavior of the systems. Although a number of experimental studies is carried out to explore various aspects of the catalytic distillation, theoretical process analysis through computer simulations has still drawn numerous research activities as they can be applied for investigating and designing catalytic distillation processes in more detail.

In order to achieve such the objective, a reliable model of the catalytic distillation is required [4]. Generally, models of the catalytic distillations can be classified into two types, according to their different complexities for explaining mass transfer and chemical reaction. The equilibrium stage model assumes that vapor and liquid streams leaving a tray or a packing segment are in thermodynamic equilibrium with each others [5]. The rate-based model (non-equilibrium model), on the other hand, implies that the vapor and liquid phase equilibrium occurs at the interface and actual rates of multicomponent interfacial mass and heat transfer

and chemical reactions are directly taken into account [6]. Comparison of the two models for packed and tray catalytic distillation columns was carried out by Peng et al. [4] and Lee and Dudukovic [7], respectively. They found that the results predicted by the two models were in good agreement. However, the rate-based model is more complex than the equilibrium model and its solution is more difficult to converge. Recently, commercial software packages, i.e., Aspen Plus and HYSYS, are widely used for the simulation studies of a catalytic distillation in many reaction systems as well. The advantage of using predefined modules in sequential simulators is that the computational time required to obtain the solution is shorter. However, the capability to modify the predefined modules for testing the validity of various assumptions is often limited and there is less flexibility when solution convergence is confronted.

The aim of this work is focused on theoretical analysis of a catalytic distillation via simulation using an equilibrium catalytic distillation model. Esterification of acetic acid with ethanol for the production of ethyl acetate is studied. Thermodynamic non-idealities of the phase equilibrium described by the UNIFAC activity coefficient model are considered. An iterative algorithm through the modified bubble-point method is employed to solve a set of nonlinear algebraic equations derived from the process models. Simulations by using the Radfrac module from Aspen Plus software are also carried out. Validation of the equilibrium model is performed by comparing the results predicted from the model with those from Aspen Plus simulator. The derived model of the catalytic distillation is further employed to study the influence of various operating parameters including reflux ratio and boilup ratio on the performance of the catalytic distillation column.

## 2 Mathematical Model of Catalytic Distillation

The typical configuration of a catalytic distillation with multi-feed streams consists of a total of  $N$  stages numbering from the top. The total condenser and the partial reboiler as defined in stage 1 and  $N$ , respectively, are used in simulations. It should be noted that as a general configuration, chemical reactions are assumed to be occurred in all the column stages; however, the different specification of the location of the reaction section can be determined according to the specific cases studied.

In this work, an equilibrium model is applied for the computer simulation of a tray catalytic distillation column. Chemical reactions described by a kinetically controlled model are assumed to occur in the liquid phase of the reaction stages. The UNIFAC activity coefficient model is utilized for describing the non-ideality of the vapor and liquid phase equilibrium. A constant pressure and adiabatic column together with perfect tray efficiency are assumed. Based on these assumptions, the model equations of the catalytic distillation column in terms of vapor and liquid molar flow rates are expressed as follows:

*Stage 1* (a total condenser)

$$V_2 y_{i,2} - (L_1 + U_1) x_{i,1} + v_i W_C r_{i,1} = 0 \quad (1)$$

$$V_2 h_{V_2} - (L_1 + U_1) h_{L_1} - Q_C = 0 \quad (2)$$

*Stage  $j$*  (a reaction stage);  $j = 2, \dots, N-1$

$$L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} + F_j z_{i,j} - (L_j + U_j) x_{i,j} - V_j y_{i,j} + v_i W_j r_{i,j} = 0 \quad (3)$$

$$L_{j-1} h_{L_{j-1}} + V_{j+1} h_{V_{j+1}} + F_j h_F - (L_j + U_j) h_{L_j} - V_j h_{V_j} = 0 \quad (4)$$

*Stage  $N$*  (a partial reboiler)

$$L_{N-1} x_{i,N-1} - L_N x_{i,N} - V_N y_{i,N} + v_i W_R r_{i,N} = 0 \quad (5)$$

$$L_{N-1} h_{L_{N-1}} - L_N h_{L_N} - V_N h_{V_N} + Q_B = 0 \quad (6)$$

Vapor and liquid phase equilibrium:

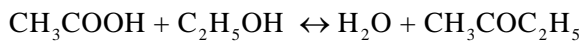
$$K_{i,j} = \gamma_{i,j} \frac{P_{i,j}^{sat}}{P_j} = \frac{y_{i,j}}{x_{i,j}} \quad (7)$$

where  $y$  and  $x$  are the mole fraction of substances in the vapor and liquid phase,  $L$  and  $V$  are liquid and vapor flow rate,  $i$  and  $j$  are the index that represents the component and the column stage, and  $U$  is the liquid flow rate of side streams (note that the flow rates of distillate and bottom products are designated as  $U_1$  and  $U_N$ , respectively).

It is interesting to be noted that for low to moderate pressure, the modified Raoult's law (Eq. (7)) coupled with the activity coefficient calculated using UNIFAC model can be reasonably used in order to take into account the non-ideality of the vapor and liquid phase equilibrium relation, and that since enthalpy balances, Eqs. (2), (4), (6), are calculated based on enthalpies of formation at standard condition, the heat of reaction is implicitly included in the energy balance equations.

## 2.1 Kinetic model for the synthesis of ethyl acetate

Ethyl acetate is one of the widely used commodity chemicals. It is primarily utilized as a solvent for paints and coatings, printing inks, adhesives and cosmetics and generally produced by the esterification reaction of ethanol with acetic acid as shown in the following stoichiometric equation,



It can be seen that the esterification is a typical example of reversible and equilibrium-limited reactions which is beneficial for applying to a catalytic distillation system as continue separation of products from reactants during the course of the reaction can shift the chemical equilibrium forward, resulting in a higher conversion.

Two different kinetic expressions of the esterification of ethanol with acetic acid to produce ethyl acetate as reported by Alejski and Duprat [8] are incorporated in the model of the catalytic distillation column, which is developed in the previous section. On stages with sulphuric acid as catalyst, the rate equations can be expressed in terms of concentrations as follows,

$$r_1 = k_1 C_1 C_2 - \frac{k_1}{K_c} C_3 C_4$$

$$k_1 = (4.195v_k + 0.08815) \exp\left(\frac{-6500.1}{T}\right)$$

$$K_c = 7.558 - 0.012T$$

On stages without catalyst, the rate equations for esterification are given below:

$$r_2 = k_2 C_1 C_2 - k_3 C_3 C_4$$

$$k_2 = 0.485 \exp\left(\frac{-7186}{T}\right)$$

$$k_3 = 0.123 \exp\left(\frac{-7186}{T}\right)$$

where  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  denotes the concentration of acetic acid, ethanol, water, and ethyl acetate, respectively.

## 3 Numerical Solution

As seen from the earlier section, the mathematical model described the steady state behavior of a catalytic distillation comprises of a set of nonlinear algebraic equations. In this work, a sequential solution procedure via the modified bubble-point

method is proposed in order to solve the derived model equations. The detailed calculation algorithm is summarized as given below:

(1) Specify all the common specification variables of a catalytic distillation column.

(2) Initialize the vapor flow rate  $V_j$  by assuming constant molar flow and calculate corresponding liquid flow rate  $L_j$ .

(3) Initialize the column temperature  $T_j$  at each stage.

(4) Calculate the liquid mole fraction  $x_{i,j}$  from material balance equations coupled with the vapor-liquid equilibrium relation and normalize the value of  $x_{i,j}$ .

(5) Calculate the vapor mole fraction  $y_{i,j}$  from the vapor-liquid equilibrium relation and normalize value of  $y_{i,j}$ .

(6) Calculate a new set of the temperature  $T_j$  from the normalized value of  $x_{i,j}$  through the solution of the bubble point expression.

(7) Calculate a new set of the vapor flow rate  $V_j$  from energy balance equations using the new set of the temperature  $T_j$  computed from step 6.

(8) Examine the convergence criterion, Eq. (8). If satisfied, the solution is terminated; otherwise, go back to step 4 and repeat the calculation.

$$\sum_{j=1}^N (T_j^{(k)} - T_j^{(k-1)})^2 \leq 0.01N \quad (8)$$

The proposed computational procedure is implemented into the high-level languages environment Matlab 6.5. The set of nonlinear algebraic equations that arise from steps 4, 6, and 7 is numerically solved using a nonlinear program (NLP) based on an efficient trust-region dogleg algorithm in Matlab optimization toolbox. It has been found from simulations that the algorithm used shows good convergence and robustness properties, although it takes longer computational time compared to Aspen Plus simulator. Additionally, it is noticed that the initial guess of vapor molar flow rates in each stage of the column seems to be the important step affecting whether the solution is converged.

## 4 Simulation Results and Discussion

The equilibrium model of a catalytic distillation column in conjunction with the kinetically controlled esterification model is applied for the simulation studies of the synthesis of ethyl acetate. Four components are concerned with this process, namely, ethyl acetate, ethanol, water and acetic acid, which have the boiling point at atmospheric pressure as follows: 77.2 °C, 78.3 °C, 100.0 °C, 118.0 °C,

respectively. The aim of the simulations is to compare the accuracy of the developed model with Table 1. The column specifications

Column conditions		
reflux ratio	1.5	
boilup ratio	0.75	
liquid holdup of condenser ( $W_C$ )	0.3 m <sup>3</sup>	
liquid holdup of stage $j$ ( $W_j$ )	0.3 m <sup>3</sup>	
liquid holdup of reboiler ( $W_R$ )	1.0 m <sup>3</sup>	
column pressure	101.3 kPa	
catalyst volume fraction ( $v_k$ )	0.4	
Feed conditions		
	Stream $F_1$	Stream $F_2$
stage location	4	14
temperature (K)	340	340
flow rate (mol/min)	46.336	53.664
mole fraction ( $z_i$ )	0.952/0	0/0.822
(acetic acid/ethanol/water/ ethyl acetate)	/0.048/0	/0.178/0

the Radfrac module of Aspen Plus under various conditions and to use the derived model for studying the steady-state behavior of the catalytic distillation.

The catalytic distillation column studied here consists of 25 stages including a total condenser (stage 1) and a partial reboiler (stage 25). The reaction section is represented by 11 catalytic stages (stage 4-14). Two feed streams are separately introduced to the column; the acetic-acid-rich stream (95.2 mol%) is fed into the stage located between rectifying and reaction section (stage 4) and the ethanol-rich stream (82.2 mol%) is fed into the stage located between reaction and stripping section (stage 14). The molar feed ratio of acetic acid to ethanol is unity. Liquid side streams are drawn from the condenser and the reboiler as distillate and bottom products. Typical specifications and conditions for the catalytic distillation column under the standard condition are shown in Table 1.

To examine the reliability of the developed model, simulations by using the Radfrac module from Aspen Plus simulator are carried out. The predicted results from the model are then compared with those from Aspen Plus software under the same conditions. Fig. 1 shows the liquid mole fraction of each component with the column stage number under the standard condition. The composition profiles calculated from the developed model agree well with the Aspen Plus. As shown in Fig. 1, the mole fraction of acetic acid, the heaviest components of the system, in the reaction zone decreases when it moves from the feed stage (stage 4) toward the bottom of the column. This is expected because acetic acid reacts with ethanol, which moves in the opposite direction, to form ethyl acetate and water. It can be seen from Fig. 1 that the

distillate consists of mostly ethyl acetate and water while the mole fractions of ethanol and acetic acid

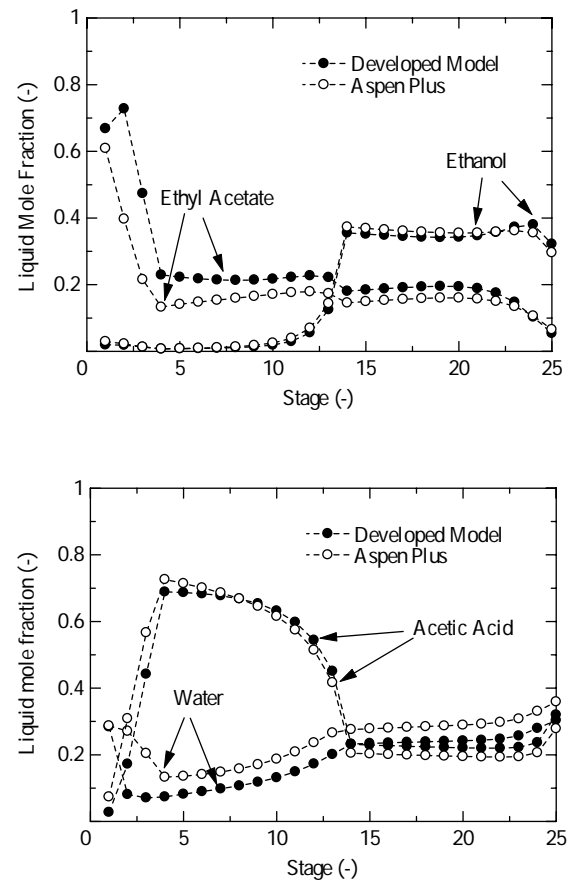


Fig. 1. Comparison of the composition profiles obtained from the developed model and Aspen Plus

negligible. The bottoms consist of mainly acetic acid, ethanol and water with a slight amount of ethyl acetate. The corresponding conversion of acetic acid and the distribution of ethyl acetate in distillate obtained from the model are 41.26% and 76.36%, respectively, while the results calculated by Aspen Plus gives slightly higher values of the conversion (48.50%) and the product distribution (78.76%).

It is noticed that a low conversion of acetic acid can be observed since ethanol, one of reactants, has a relatively high volatility; its composition in the liquid phase where esterification takes place is kept low. As a result, the rate of ethyl acetate production is decreased. This suggests that longer residence time in each stage would be required to improve the conversion of acetic acid. It should also be noted that the system consisting of ethyl acetate, ethanol, water and acetic acid can form three binary azeotropes and one ternary azeotrope; therefore, it is difficult to obtain a high purity of ethyl acetate product at the top of the column. However, the use

of a feed with a large excess of acetic acid is one possibility to achieve the desired purity [9].

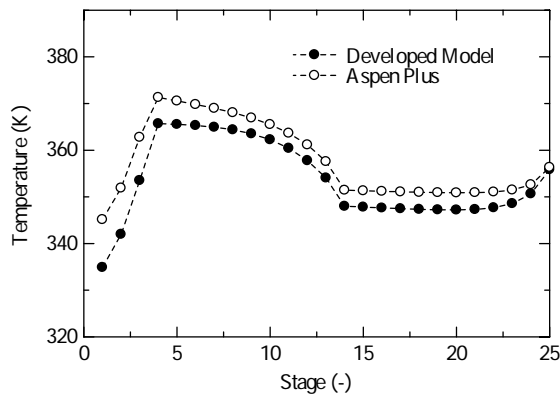


Fig. 2. Comparison of the temperature profiles obtained from the developed model and Aspen Plus.

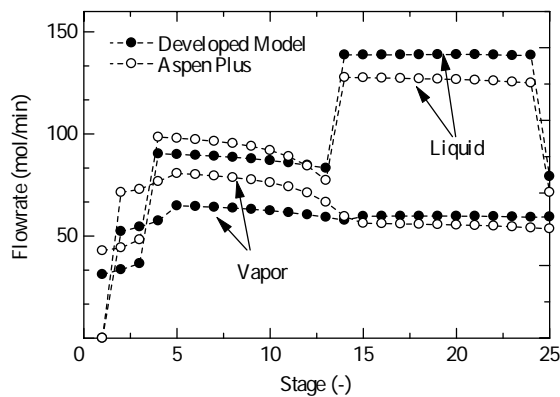


Fig. 3. Comparison of the profiles of liquid and vapor flow rate obtained from the developed model and Aspen Plus.

Comparisons of the profiles of temperature and the liquid and vapor flow rates are presented in Figs. 2 and 3. Again, the agreement between the result from the developed model and Aspen Plus is in general satisfactory; however, some differences can be observed. These may be due to the dissimilarities of the correlations used in the developed model and Aspen Plus for computing physical and thermodynamic properties.

Further, the developed model is used to analyze the influence of various operating parameters including reflux ratio and boilup ratio on the performance of the catalytic distillation.

Fig. 4 shows the effect of reflux ratio on the conversion of acetic acid and the distribution of ethyl acetate. It is found that increasing the reflux ratio from 1 to 10 results in lower conversion and product distribution. This can be explained by the fact that since ethyl acetate is the main component in

the distillate, the concentration of ethyl acetate in the reaction section is increased with high reflux ratio

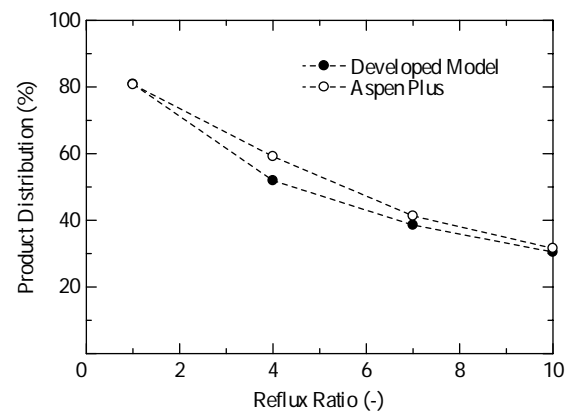
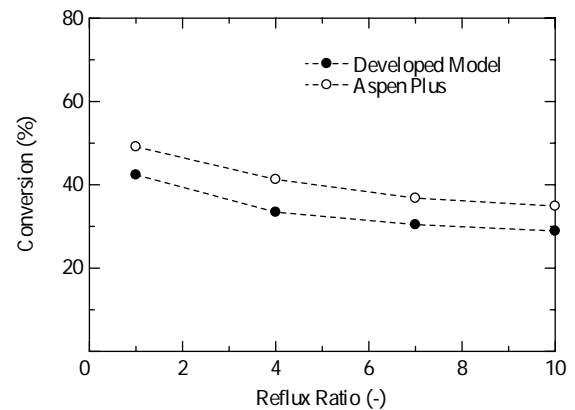


Fig. 4. Influence of reflux ratio on the conversion of acetic acid and the distribution of ethyl acetate.

and therefore, the rate of the reverse reaction is more pronounced. This causes a decrease in both the conversion of acetic acid and the amount of ethyl acetate in distillate.

Fig. 5 shows the performance of catalytic distillation as a function of the boilup ratio. It can be seen that when the boilup ratio is increased, the acetic acid conversion and the ethyl acetate distribution are improved. Since increasing the boilup ratio makes ethyl acetate more removable from the reaction section due to significant vapor load in the column. Decreasing the concentration of ethyl acetate in the liquid mixture causes the reaction equilibrium to shift in the forward direction and thus, the conversion of acetic acid becomes higher and more ethyl acetate in distillate is obtained.

It is noted that the simulations shown in Figs. (4)-(5) compare the predicted results from the developed model with those from Aspen Plus as well. Under the cases studied, the effects of several

operating parameters on the catalytic distillation obtained from both the derived model and Aspen

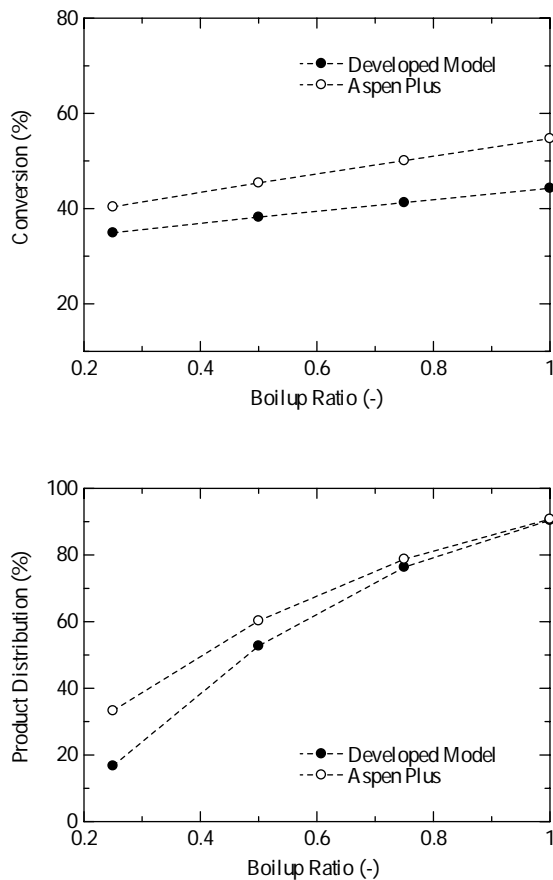


Fig. 5. Influence of boilup ratio on the conversion of acetic acid and the distribution of ethyl acetate.

Plus follow the similar trend. This demonstrates the reliability of the model to predict the behavior of the catalytic distillation system. Other applications of the developed model for design and optimization of catalytic distillation columns will be the subject of our future studies.

## 5 Conclusion

In this work, a catalytic distillation for the production of ethyl acetate from the liquid phase esterification of acetic acid with ethanol is simulated using an equilibrium stage model. The non-idealities of the liquid and vapor phase equilibrium described by the UNIFAC activity coefficient model are considered. A modified bubble-point iterative algorithm is employed to find the solution of nonlinear algebraic equations derived from the system model. The solution method has shown good convergence and robustness properties during the simulations; however, it is observed that the initial guess of the vapor molar flow rate is the crucial step

of the algorithm affecting whether the solutions are converged. Validation of the developed equilibrium model is performed by comparing with Aspen Plus. The simulations clearly show that agreement between the results predicted from the model and Aspen Plus is satisfactory. Further, the model developed is employed to study the influence of various operating parameters, i.e., reflux ratio and boilup ratio on the performance of the catalytic distillation column.

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