Simulation Studies of Reactive Distillation for Ethyl Acetate Production

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Abstract: Reactive distillation is an attractive option for equilibrium limited reactions. For highly nonideal systems, the selection of liquid phase activity model considerably influences the model predictions. In this work, activity models proposed in literature and available in RADFRAC module of Aspen Plus are compared for ethyl acetate production through reactive distillation. Also, a hybrid modelling approach, which can be easily implemented in RADFRAC, is proposed for this system. The simulation results show that the hybrid approach gives better predictions for this highly nonideal system.

Keywords: Reactive distillation, ethyl acetate, esterification.

1. INTRODUCTION

Reactive distillation (RD) involves simultaneous chemical reaction and distillation. The performance of reaction with separation in one piece of equipment offers distinct advantages over the conventional approach. In reactive distillation, chemical reactions occur within the distillation column to achieve specific goals, such as to obtain high conversions and high purity products as well to minimize side reactions. The reduction in total investment and operating cost, when reactions and separation can be carried out in the same equipment, can be substantial. However, simultaneous reactions with separation increase the modelling complexities. Taylor and Krishna have given a detailed review on reactive distillation modelling.

Reactions limited by chemical equilibrium can be shifted towards products side if the products are continuously removed from the reactor. A distillation column can be advantageously used as a reactor for systems in which chemical reactions occur at temperatures and pressures suitable to the distillation of components. Esterification of acetic acid with ethanol is an important industrial process where RD can be applied. The reaction of ethanol (EtOH) with acetic acid (AcOH) towards ethyl acetate (EtAc) and water (H_2O) is an equilibrium limited reaction. The system is strongly non-ideal due to the presence of ethanol, acetic acid, and water. In this quaternary system, azeotropes are formed between EtOH-H_2O, EtAc-H_2O, EtAc-EtOH, and EtAc-H_2O-EtOH.

Various approaches for solving the equilibrium and non equilibrium models of this RD process have been proposed in the literature [2-8]. Venkataraman et al. [9] demonstrated that RADFRAC module of Aspen Plus can be used for RD simulations. Many recent simulation studies on ethyl acetate production through RD [10-13] used RADFRAC and proved its usefulness for this complex RD process.

The selection of liquid phase activity model for this RD system considerably influences the model predictions. Thus, various liquid phase activity models have been studied for this system [8, 10, 12, 14-16]. Most works cited above have used the 11 plate column example data of Suzuki et al. [14] for comparison with their results.

In the present work, RADFRAC module of Aspen Plus is used to carry out the steady state simulations for ethyl acetate production in a RD column. The column specifications given in Simandl et al. [7] are used for the simulations. A hybrid activity model approach for the RD column, demonstrating the flexibility of RADFRAC, for the simulation of this highly non ideal system is proposed.

2. RD MODEL

In the selected reactive distillation system, acetic acid (AA) and ethanol (EtOH) form ethyl acetate (EtAc) and water (H_2O) through an equilibrium limited reaction which can be expressed in the following form

$$AA + EtOH = EtAc + H_2O$$

The reaction rate at each stage is evaluated by the equation given in [9].

Simulations are done on a 13 tray column including a reboiler and a total condenser. Stages are numbered from top to bottom. Column specifications and other data used for the simulations are given in Table 1. Ethanol and acetic acid are fed into the column that operates near atmospheric pressure. Acetic acid being heaviest component moves towards the bottom of the column. Other three components (ethyl acetate, ethanol, and water) move towards the top of the column.

Table-1: Column specifications and other parameters used for RADFRAC simulations [7]

Total Stages	13 (including Reboiler and condenser)
Number of components, c	4
Column Pressure	1 atm
Feed Stages	6 (from top)
Feed rate (mol/min)	0.1076
Distillate Rate(mol/min)	0.0208
Holdup	1 l for reboiler, 0.3 l for each stage
Feed Composition:	
Acetic Acid Ethanol Water Ethyl acetate	0. 4963 0.4808 0.0229 0.0
Reflux Ratio	10

For modelling an equilibrium stage in reactive distillation, MESH (material balance, energy balance, summation, and enthalpy balance) equations with reaction term are used. RADFRAC uses inside-out method for the solution of model equations. In this method the complex physical properties are approximated by simple models in the outer loop while MESH equations are solved in the inner loop [9].

3. RESULTS AN DDISCUSSION

Okur and Bayramoglu [8] in their RD simulation study have used UNIQUAC, UNIFAC (Dortmund), UNIFAC (Lyngby) and empirical [14] methods for liquid phase activity model. Pilavachi et al. [10] in their simulations tried UNIQUAC, UNIFAC, and Wilson models. Therefore, in the present work, simulations are run for various activity models, available in Aspen Plus, and the results for ethyl acetate composition are compared with the experimental data of Komatsu et al. [18]. The results for liquid phase ethyl acetate composition are presented in Fig. 2. Vapor phase for these simulations is modeled either by SRK, HOC, or Ideal model.

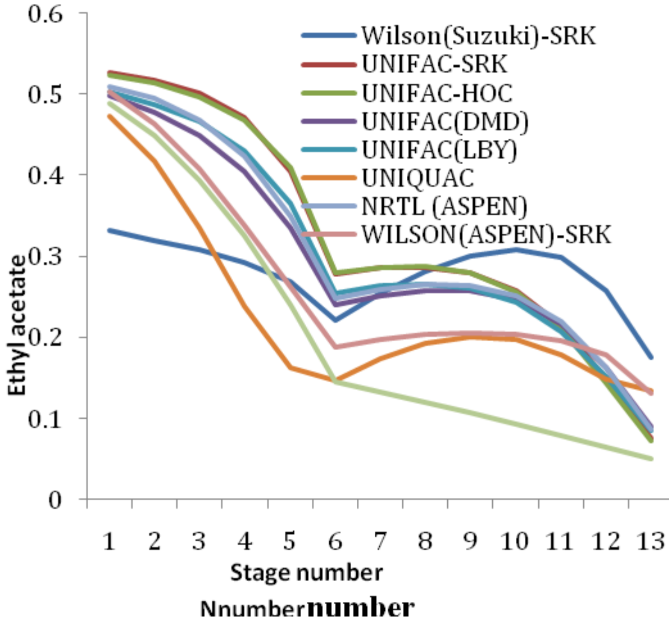

Fig. 2: Comparison of simulation results with the data of Komatsu et al. [18]

Results show that the Wilson model for liquid phase activity with SRK model for vapor phase, and UNIQUAC model predict the experimental data more closely as compared to other models. However, in the lower part of the column the match is poor even with these models. The results show that the K values for acetic acid and water are better predicted by UNIQUAC model and K values of ethanol and ethyl acetate are better predicted by the Wilson model (Fig. 3 a-d). However, the match is poor in the lower portion of the column for both the models. This explains the poor match of ethyl acetate composition in the lower portion of the column (Fig. 2).

A hybrid activity model approach was tried to improve the simulation results.The RD column was divided into two segments (segment 1: stage 1-6; segment 2: stage 7-13), and a different activity model in each segment was used. The combination of UNIFAC model for the top segment and Wilson model for the bottom segment gave the best results. Hayden and O'Connell model was used for the vapor phase. Comparison of simulation results with the experimental data for liquid phase composition of ethyl acetate is shown in Fig. 4. The results show that the hybrid model approach has improved the simulation predictions in the lower portion of the column. The overall ethyl acetate composition profile is better predicted by this approach as compared to the single activity model approach for the entire column (Fig. 2).

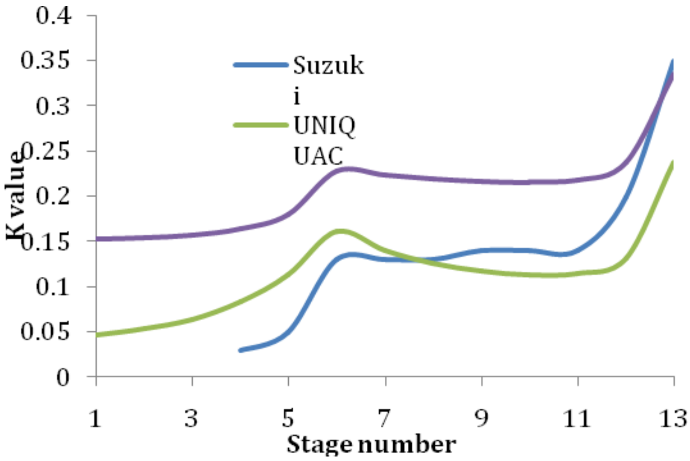

Fig. 3(a): Acetic acid K values

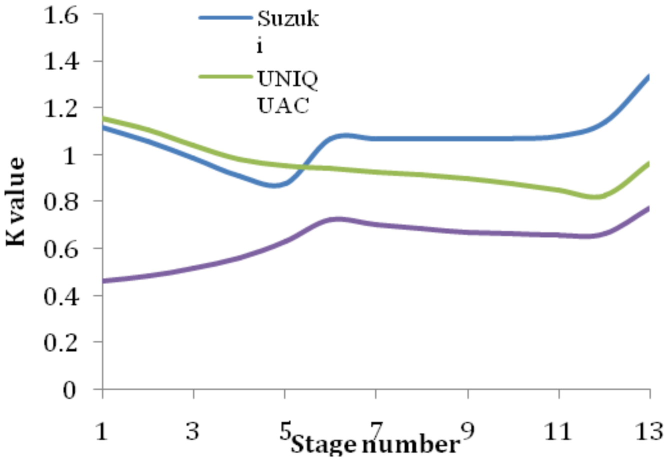

Fig. 3(b): Water K values

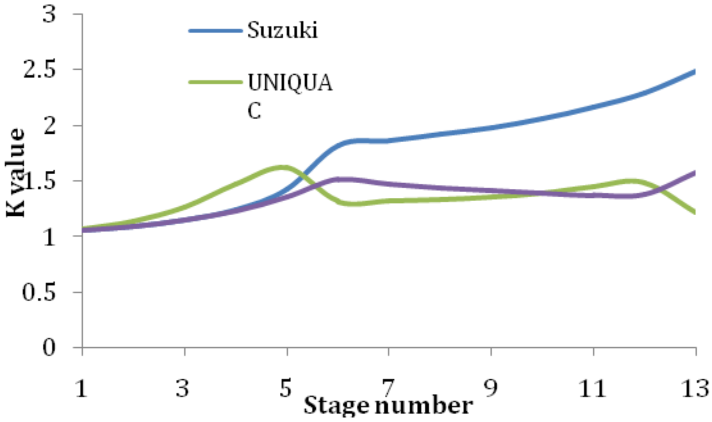

Fig. 3(c): Ethyl acetate K values

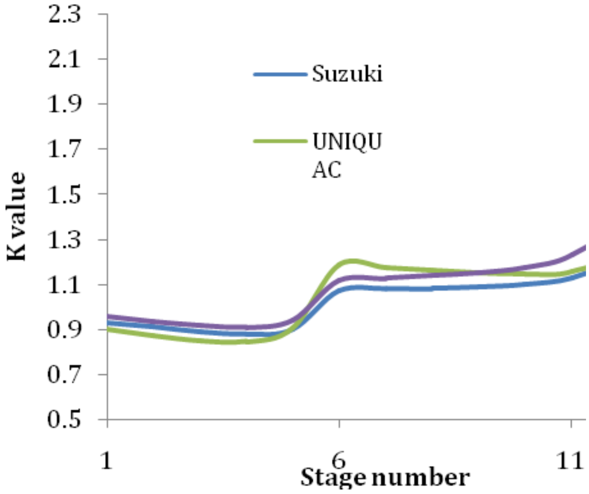

Fig. 3(d): Ethanol K values

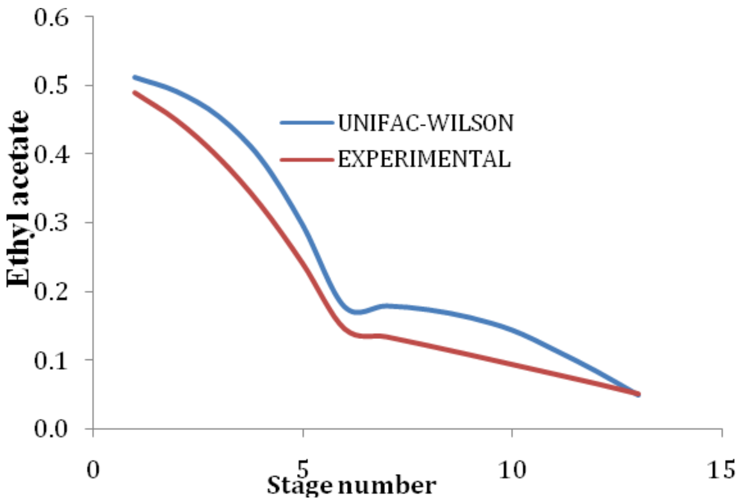

Fig. 4: Comparison of simulation results for hybrid model with experimental data [18]

4. CONCLUSION

The reactive distillation column for ethyl acetate production is simulated using RADFRAC module of ASPEN PLUS. The results show that the Wilson model for liquid phase activity with SRK model for vapor phase, and UNIQUAC model for liquid phase predict the experimental data most closely. However, in the lower part of the column even these models do not give satisfactory match. The hybrid activity model approach has improved the simulation predictions; especially in the lower portion of the column.

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