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Research Article

Modeling of Reactive Distillation Column for the production of Ethyl Acetate

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Abstract

The production of ethyl acetate is gaining lot of attention because of the growing needs of the greener fuel in the world. Reactive distillation (RD) is a column in which reactor and separator work simultaneously. Ethyl acetate is an ester produced through the reversible reactions such as esterification and etherification in reactive distillation column. In the proposed work modeling of the reactive distillation column for the production of ethyl acetate is given. The model incorporates reaction kinetics and vapor liquid non idealities balanced through MESH (Material Balance, Equilibrium Relationships, Summation equation and energy balance). Present study discussed the current modeling techniques and its importance.

Keywords: *Reactive distillation, Material Balance, Vapor-liquid equilibrium, Modeling, Feed composition*

Introduction

Reactive distillation operation has been an area of interest from last two decades. The combination of reaction and separation in a single unit is an alternative to conventional distillation which includes reaction and separation in number of units thus increases the investment cost of the plant. The three important functional areas of reactive distillation column are: (1)Distillation column consist of reactive section which leads to the conversion of reactants into products (2)It improves the separation in the column by changing the component volatilities (3)increases the selectivity of product(A. Giwa *et. al.* **,** 2012)

Literature survey

The process in which reaction zone and separation zone are coupled together is not a newer approach it was patented in 1920's and first real world implementation was done commercially in 1980's. RD has been worked upon by many researchers as Doherty and Buzad, 1992; Podrebarac *et. al*., 1997.RD is very fortunate in terms of reaction kinetics, economy, yield of product on the other hand its designing is very tedious. Complexity in designing arises due to introduction of *in situ* separation function within the reaction zone leads to intricate interaction between vapor–liquid equilibria, vapor-liquid mass transfer, intra catalyst diffusion and chemical kinetics((A. Giwa *et. al.* **,** 2012). Commercializing RD column

Requires very peer attention on the modeling aspects of column as column Dynamics, and the conceptual design stage (Doherty& Buzad, 1992; Roat, Downs, Vogel & Doss,1986).(Taylor, R. & Krishna, R. 2000), Thus for designing of reactive distillation column the correct model of the process is required.

In literature there are broadly two types of model approaches for RD column namely equilibrium stage model and non-equilibrium stage model or rate based model. The equilibrium stage model assumes that the vapor and liquid leaving on each stage is in equilibrium with each other. It is based on MESH equations M=material balance; E=vapor-liquid equilibrium; S=mole fraction summation and H=heat balance [1]. On the other hand non equilibrium model is a more realistic approach based on the assumption that the vapor-liquid equilibrium is established at the interface between the liquid and the vapor phase and the flux is calculated by employing transport based approach.

Modeling

The esterification of acetic acid with ethanol towards ethyl acetate and water occurs according to the reaction.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

(S. R.Lone *et. al*., 2012)

A. Assumptions taken

- The holdup of vapor on each stage is negligible as compared to liquid holdup.
- Chemical reactions are assumed to occur only in liquid phase.
- Volumetric holdup on each stage in condenser and in re-boiler is assumed to be constant.
- There is no pressure drop in the column.
  Heat generated during the chemical is taken into account.

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- Vapor phase is assumed to be ideal gas.
- There is perfect level control in the reflux drum.
- No sub-cooling in the condenser is assumed.

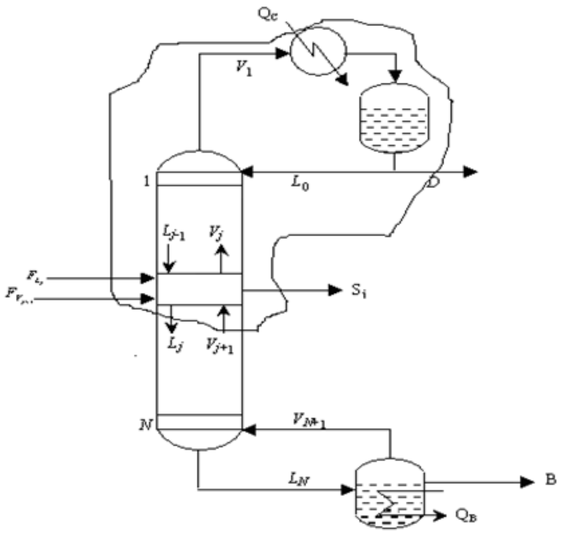

Fig.1 Schematic diagram of RD Column

B. Mass and Energy Balance

Overall mass and energy balance around the loop of column is given by:

$$V_{j+1} - L_j = D - \sum_{k=1}^{j} F_{L_k} - \sum_{k=1}^{j+1} F_{V_k} + \sum_{k=1}^{j} S_k - \sum_{k=1}^{j}\sum_{i=1}^{N_C} W_k R_{ki} \equiv RHS_1 \quad (1.1)$$

$$V_{j+1}H_{V\,j+1} - L_j H_{L\,j} = DH_D + Q_C - \sum_{k=1}^{j} F_{L_k} H_{FL\,k} - \sum_{k=1}^{j+1} F_{V_k} H_{FV_k} + \sum_{k=1}^{j} S_k H_{L_k} - \sum_{k=1}^{j} Q_k - \sum_{k=1}^{j} W_k R_{k,ref}(-\Delta H_{R_{k,ref}}) \equiv RHS_2 \quad (1.2)$$

$$V_{j+1} = RHS_1 + L_j \quad (1.3)$$

$$L_j = \frac{RHS_2 - RHS_1 \times H_{V_{j+1}}}{H_{V\,j+1} - H_{L\,j}} \quad (1.4)$$

Basic mathematical model consists essentially of mass and energy balances around three sections of the column as shown in Fig. 3, namely, the condenser-reflux drum (denoted by suffix 0), an arbitrary plate (denoted by suffix *j)*, and the reboiler (denoted by suffix *N+1*), together with the equilibrium relationships and other equations of state. For the condenser-reflux drum system, the total mass balance and component wise mass balance equations are

$$\frac{d(M_D)}{dt} = V_1 - L_0 + D \quad (1.5)$$

As per our assumption of constant molar holdup in reflux drum, the component mass balance around reflux drum is

$$M_D \frac{dx_{D_i}}{dt} = V_1 y_{1,i} - (L_0 + D)x_{D_i} \;\; (i = 1 \text{ to } c) \quad (1.6)$$

Enthalpy balance around the condenser-reflux drum yields

$$Q_C = V_1\left(H_{V_1} - H_{L_0}\right) + W_0 R_{0,ref}\left(-\Delta H_{0,ref}\right) \quad (1.7)$$

For an arbitrary plate j ($1 \le j \le N$) in the column, the total mass balance, the component-wise mass balance and the enthalpy balance yield respectively,

$$L_{j-1} + V_{j+1} - L_j - V_j + F_{V_{j+1}} + \sum_{i=1}^{j} W_j R_{j,i} = \frac{d(M_j)}{dt} \quad (1.8)$$

Assuming molar holdup on each tray to be constant, the component balance as

$$M_j \frac{d(x_{j,i})}{dt} = L_{j-1}x_{j-1,i} + V_{j+1}y_{j+1,i} + F_{L_j} z_{fl\,j,i} + F_{V_{j+1}} z_{fv\,j+1,i} - L_j x_{j,i} - V_j y_{j,i} - S_j x_{j,i} + W_j R_{j,i} \quad (1.9)$$

Total mass and component balance on the Reboiler.

$$\frac{dM_B}{dt} = L_N - V_{N+1} - B + \sum_{i=1}^{j} W_{N+1} R_{N+1,i} \quad (1.10)$$

Assuming molar hold up to be constant in reboiler, the component mass balance around re boiler is

$$M_B \frac{dx_{N+1,i}}{dt} = L_N x_{N,i} - V_{N+1} y_{N+1,i} - B x_{N+1,i} + W_{N+1} R_{N+1,i} \quad (1.11)$$

Enthalpy balance around re boiler is,

$$Q_B = B_N - L_N H_{N_L} + V_{N+1} H_{V_{N+1}} - W_{N+1} R_{N+1,ref}\left(-\Delta H_{R,ref}\right) \quad (1.12)$$

C. Equilibrium Relationship

The most commonly used vapour-liquid equilibrium relation is modified Raoult's law, which is valid for low to moderate pressure:

$$y_i P = x_i \gamma_i P_i^{sat} \qquad (i = 1 \text{ to } c) \quad (1.13)$$

Activity coefficients γ_i were calculated from NRTL equation. The vapour compositions and stage temperatures are obtained from the bubble-point calculation using Newton–Raphson technique. The individual values of $y_{j,i}$ and $x_{j,i}$ should satisfy the equation below:

$$\sum_{i=1}^{c} y_{j,i} = 1.0 \;\; (j = 1,...N+1) \; ; \quad \sum_{i=1}^{c} x_{j,i} = 1.0 \;\; (j = 0,...N+1) \quad (1.14)$$

D. Reaction Kinetics

Acetic acid reacts with ethanol in the presence of an acid catalyst to give ethyl acetate and water.

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

The reaction rate can be written as follows:

$$r = k_1C_1C_2 - k_2C_3C_4 \quad (1.15)$$

The rate constants k_1 and k_2 are given as under:

$$k_1 = 4.76*10^4 \exp(-59774(J/gmol)/RT) \quad (1.16)$$

$$k_2 = 1.63*10^4 \exp(59774(J/gmol)/RT) \quad (1.17)$$

Results and Discussions

For the validating the model the compositions of the top bottom segment product compositions were considered because they were the ones used to determine the nature of the desired product (ethyl acetate) obtained.

The data having the column configuration, feed composition, column holdup etc. are taken from Mujtaba & Macchietto (1997) as given in Table 1.

At reflux ratio 10 the composition profile in the column at steady state is shown in Fig.2. In this figure, it is clear that the ethyl acetate is mostly concentrated in the top plate and become highest as top product, acetic acid concentration increases from top to feed plate, becomes almost same from feed plate to plate no.10 and then again increases and gets collected in the bottoms. Ethanol concentration increases from bottoms to feed plate and then decreases above plate no. 4. Water concentration is not much affected.

A. Optimum feed composition

The steady state values of ethyl acetate composition in top product obtained at several EtOH/AA ratios are shown Fig3. It is clear from this figure that as EtOH/AA ratio is increased, the ethyl acetate composition increases, reaches to a maximum value of 0.4471 at EtOH/AA ratio of 0.476 and then falls down. Therefore the optimum EtOH/AA ratio is found to be 0.476

All the data used for RD column specifications are based on experimental results these results are to be validated for the model proposed.

Table1: Column Specification Data for Ethanol Esterification

Number of ideal stage (including re boiler and condenser)	14
Total fresh feed	0.00179 mol/s
Feed composition (Acetic Acid, Ethanol, Water, Ethyl Acetate,) in mole fraction	0.4962, 0.4808, 0.0240, 0
Distillate rate, D	0.0004464 mol/s
Condenser holdup	0.4 liter
Re boiler holdup	1.0 liter
Each internal plate holdup	0.4 liter
Column pressure	1.01425 bar
Feed plate No.	6
Reflux Ratio (L/D)	10
Bottoms rate, B	0.0014446 mol/s

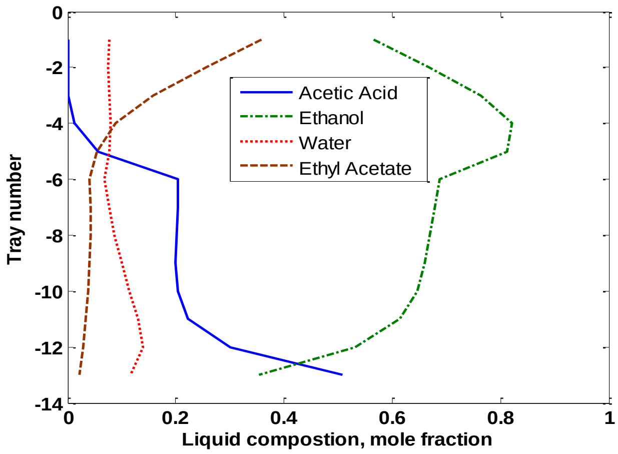

Fig.2 Composition Profile in the Colum

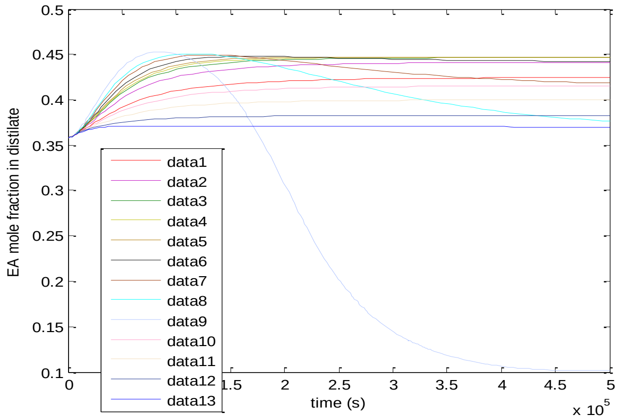

Fig. 3 Simulation results for the best feed composition

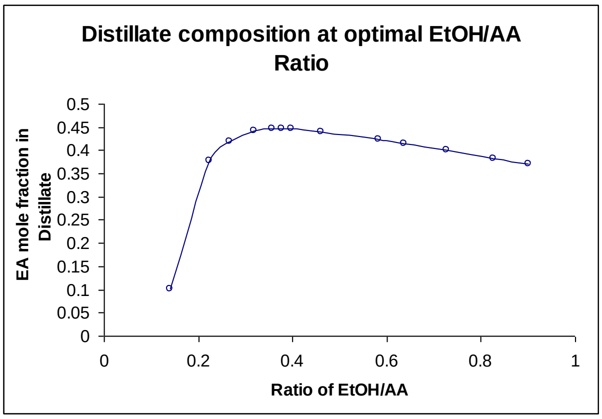

Fig. 4 Distillate composition for different EtOH/AA ratio

Conclusions

The outcomes obtained from this study have shown that there were fine agreements between the top and bottom compositions estimated theoretically and one obtained from MATLAB simulation developed for the reactive distillation for the validity of the model equations. Therefore, the developed models have been found to be suitable in representing the reactive distillation column very well.

Notations

Q_B Total re boiler heat duty (J)
$h_{fg,}$ Latent heat of vaporization of component i (J/mol) Heat of reaction (J/mol)
H_L Liquid enthalpy (J)
H_V Vapor enthalpy (J)
L_j Liquid flow rate from j^{th} plate (mol/s)
Q_C Heat duty on condenser-reflux drums (J/s)
Q_{N+1} Heat duty on condenser-reflux drum (J/s)
$R_{j,j}$ Rate of reaction of i^{th} component on j^{th} plate(s^{-1})
$x_{j,i}$,$y_{j,i}$ Mole fraction of i^{th} component in liquid phase and vapour phase respectively on j^{th} plate.

Subscripts

RD Reactive Distillation
AA Acetic Acid
EtOH Ethanol
EA Ethyl Acetate
W Water

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