Modeling and Simulation of Reactive Distillation Column for Esterification of Isoamyl Alcohol and Acetic Acid

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Abstract—*There is an increasing trend of chemical industries toward new processes that should meet requirements such as generation of nearly zero waste chemicals, less energy, and sufficient uses of product chemicals in various applications. The reactive distillation provides an attractive alternative for reaction/separation processes withreversible reactions, especially for etherification and esterification. Esterification is the general name for a chemical reaction in which two reactants Iso amyl alcohol and acetic acid form an ester as a product. In the simulation, RADFRAC model was chosen to take care of the complexities arising due to simultaneous reaction and separation in a single unit. NRTL property method was selected in the simulator for equilibrium calculations.In this work, the equilibrium model for synthesis of iso amyl acetate was developed. The simulation studies were performed in Aspen Plus. The effects of the variables such as the reflux ratio, boil up ratio, feed flow rate and feed plate locations etc. are important in RD process. Therefore the results of sensitivity studies for these variables are discussed using Aspen Plus® to see the optimum performance of RD column.*

Keywords: *Reactive distillation, esterification, EQ model, Aspen Plus simulation, sensitivity studies.*

1. INTRODUCTION

Reactive distillation (RD) is a combination of reaction and distillation in a single vesselowing to which it enjoys a number of specific advantages over conventional sequentialapproach of reaction followed by distillation or other separation techniques. Improvedselectivity, increased conversion, better heat control, effective utilization of reaction heat,scope for difficult separations and the avoidance of azeotropes are a few of theadvantages that are offered by RD [1].

RD for many different processes has been rapidly implemented in more than 150 commercial operation of the petrochemical and chemical industry. Iso amyl acetate has been used in the industry as a solvent, andextractants, and polishing agent. It is used as artificial flavoring in banana-flavoredbubble gums, as preservative in sodas and soft drinks as well as artificial scent forcovering unpleasant odors.It is also used in large quantities in artificially pear- flavored food articles as additive in cigarettes, and asnitrocellulose, lacquers, celluloid, and camphor. It is also used to manufacture celluloid cements, water proof varnishes, artificial silk, leather or pearls, photographic films, bronzing liquids andmetallic paints, perfuming shoe polishes and dyeing and finishing textiles [4].

2. WHY RD?

The two reactants, acetic acid and amyl alcohol, are intermediate boilers, whereas the products, water and Isoamyl acetate, are low and high boilers respectively. As Isoamyl acetate and water are the heaviest and lightest boiling substances respectively in the quaternary system, they can be continuously removed from the reaction zone in a RD column so that high conversions can be achieved, thus RD an attractive process for producing iso-amyl acetate. That's why reactions (1) are well suited for reactive distillation [5].

RD is promising and cost-effective method of separation for the recovery of dilutes acetic acid from its aqueous streams. Moreover, a value added product in the form of Iso-amyl acetate is produced during recovery of acetic acid by esterification with iso-amyl alcohol [3].

Table 1: Boiling points of the components

Components	Boiling points(°C)
Acetic Acid	118
Iso amyl Alcohol	137.8
Iso amyl acetate	148.8
Water	100

3. MATHEMATICAL MODELING

The esterification of acetic acid (with isoamyl alcohol) is considered inside a RD column. The column has a total condenser and a Reboiler. The theoretical stages are numbered

from top to bottom. The condenser is represented by stage 1 and Reboiler is represented by stage 27.

3.1 Model Assumptions

1. The various assumptions made during the development of model were as follows:
2. The vapor and liquid on each plate and leaving on each plate are perfectly mixed. Moreover, the liquid on the plate has the same compositions as the liquid leaving the plate.
3. Constant molar liquid holdup is assumed for each stage.
4. Molar vapor holdup is negligible in comparison with the molar liquid holdup.
5. Simple or complex reaction(s) proceed only in the liquid phase and their rate can be described by an appropriate kinetic expression.
6. The liquid phase is in equilibrium with the vapor phase leaving the plate.

The assumptions above lead to a model that consists of a set of ordinary differential and algebraic equations (DAE's) [2]. From the mass and energy dynamic balances on the jth plate according to Fig. 1, the model is derived as follows:
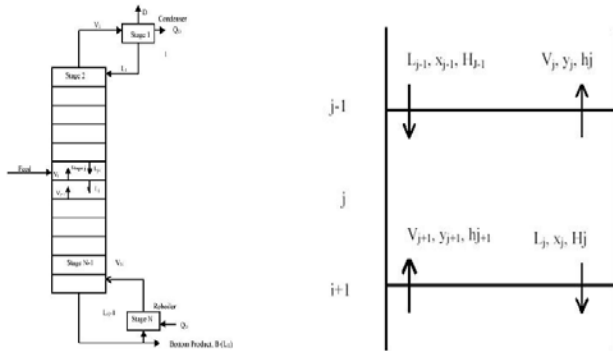

Fig. 1: Single stage (j) in the column showing the corresponding streams

The Mass balance of component i around plate j is given by:

$$\frac{d(x_{i,j}M_j)}{dt} = V_{j+1}y_{i,j+1} - L_j x_{i,j} + L_{j-1}x_{i,j-1} - V_j y_{i,j} + \Delta R_{i,j} \quad (1)$$

$$\frac{dx_{i,j}}{dt} + M_j + \frac{dM_j}{dt}x_{i,j} =$$
$$V_{j+1}y_{i,j+1} - L_j x_{i,j} + L_{j-1}x_{i,j-1} - V_j y_{i,j} + \Delta R_{i,j} \quad (2)$$

This is combined with overall mass balance around plate J:

$$\frac{dM_j}{dt} = V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j \quad (3)$$

The subscripts " i" range in value from 1 to the number of components in the mixture. The subscripts j ranges in value from 1 to the number of plates, N.

The Equilibrium equation:

$$y_{i,j} = K_{i,j}x_{i,j} \quad (4)$$

where K= equilibrium constant

giving;

$$\frac{d(x_{i,j})}{dt}M_j = V_{j+1}K_{i,j+1}x_{i,j+1} - L_j x_{i,j} + L_{j-1}x_{i,j-1} - V_j K_{i,j}x_{i,j}$$
$$+ \Delta R_{i,j} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j)x_{i,j} \quad (5)$$

The Energy balance equation around the plate j is given by:

$$\frac{d(H_{i,j}M_j)}{dt} = V_{j+1}h_{i,j+1} - L_j H_{i,j} + L_{j-1}H_{i,j-1} - V_j h_{i,j} \quad (6)$$

$$\frac{dH_{i,j}}{dt}M_j + \frac{dM_j}{dt}H_{i,j} = V_{j+1}h_{i,j+1} - L_j H_{i,j} + L_{j-1}H_{i,j-1} - V_j h_{i,j} \quad (7)$$

This is combined with overall energy balance around plate J:

$$\frac{dH_{i,j}}{dt}M_j = V_{j+1}h_{i,j+1} - L_j H_{i,j} + L_{j-1}H_{i,j-1} - V_j h_{i,j} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j) + H_{i,j} \quad (8)$$

These equations are coupled with algebraic equations for reaction kinetics and vapor-liquid equilibrium.

4. PHASE EQUILIBRIA AND REACTION KINETICS DATA

The two reactants, acetic acid and 1-pentanol, are intermediate boilers, whereas the products, water and amyl acetate, are the low and high boilers, respectively. The nonrandom two-liquid (NRTL) activity coefficient model was used for the vapor-liquid liquid equilibrium. (VLLE) for the quaternary system containing acetic acid, Isoamyl alcohol, amyl acetate, and water [6].

The kinetic expressions and other data is used for simulation work is given below:

$$r = m_{cat}\ (k_1 C_{CH_3COOH} C_{C_5H_{11}OH} - C_{C_5HH_{11}COOCH_3} C_{H_2O}) \quad (9)$$

5. SIMULATION WORK

The procedure for the development of RD processes applied here can be divided into four steps. In the first step, the thermodynamic properties of the system are investigated to obtain a reliable description of liquid-phase nonideality that can be used for a preliminary feasibility analysis. Then, the reaction kinetics is investigated at conditions that are expected for the RD column. These results can be combined, and a simulation environment based on an equilibrium stagemodel can be employed. This work considers the production of iso-amyl acetate by RD. The paper is focused on identifying suitable process conditions and limitations for the synthesis of iso-amyl acetate. Simulation is used with equilibrium-stage model to identify optimum processing strategies [2].
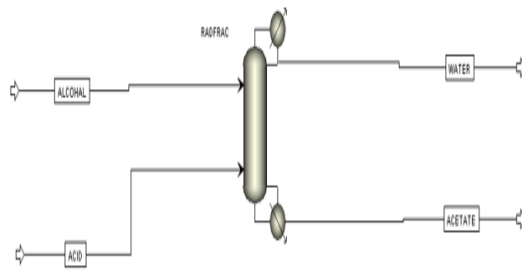
Fig. 2: Process flow sheet for Isoamyl acetate synthesis in Aspen Environment

Table 2: Design and Operating Parameters for the iso-amyl acetate

Total Number of Stages	27
Total packed height (m)	2.75m
Number of Stages (reactive)	6
Number of Stages (stripping)	12
Number of Stages (rectification)	9
Reactive zone, height (m)	1m
Stripping zone, height (m)	1m
Rectification zone, height (m)	.75m
Column diameter (m)	0.05
Reflux ratio	2
Feed location for iso amyl alcohol (Top of reactive zone)	10
Feed location for acetic acid (bottom of reactive zone)	15
Reboiler duty (KW)	1.2
Mole fraction of iso amyl acetate (bottom)	.99
Mole fraction of Water (top)	.9915

Table 3: Base specification in Aspen Plus Simulation Molar flow rates:

Sr. No.	Measurements	Value	Units
1	Feed flow rate (acetic acid)	0.03200	kmol/hr
2	Feed Flow Rate (iso amyl alcohol)	0.03500	kmol/hr
3	Mole ratio, acid/alcohol	.5384	
4	Conversion in terms of acetic acid	99.50	%
5	Bottom product Composition (mole fractions)	iso amyl acetate=.993	-
6	Top product composition(mole fractions)	Water=.9845	-
7	Purity of bottom product	98.15	%

6. SIMULATION RESULTS

In this model physical equilibrium is assumed on each stage and the reaction kinetics at each stage was described by a second order reaction. As can be seen from the simulation results as shown in Fig. (3) conversion of 99.5% of iso-amyl acetate, with iso amyl acetate purities of 88.4 % was achieved. Fig. (3) shows the mole fractions of acetic acid, iso amyl alcohol, iso amyl acetate and water in the liquid phase. In the

reaction zone (stages 10 to 15), iso amyl alcohol is consumed, and as a result, its mole fraction decreases. Stages 15 and 16 show the transition between the reaction and stripping zones in the column. In the stripping zone, iso amyl acetate and iso amyl alcohol are being separated, resulting in the higher concentration of iso amyl acetate in the bottoms. High mole fractions of iso amyl acetate are obtained in the liquid phase.

Fig. (4) shows the temperature profile obtained when the equilibrium model is employed. The reaction zone was located at the middle of the column and is comprised of stages 10 to 15. The remaining stages are pure separation stages. A smooth temperature profile is observed in the reactive zone where the catalyst is located In all the runs, the temperature in reactive zone is in the range of 120-130℃. Sufficiently high temperature ensure reaction to be at the chemical equilibrium and driven by distillation.The temperature and composition profiles for this system from the equilibrium model are compared with experimental data under the same conditions [1].

7. SENSITIVITY STUDIES

Fig. (5) shows effect of boil up rate on purity of top product. It was observed that as boil up increases, the purity of top product also increases. From Fig. (6) it is clear that as we increase the reflux ratio, the top product purity also increases, following linear relation. Fig. (7) and (8) depict effect of feed plate location on top product purity. It was observed that feed stage 10 for acetic acid and feed stage 15 from Isoamyl alcohol is the best-feed locations for optimum RD column performance [1].

8. CONCLUSION

The equilibrium model for synthesis of iso amyl acetate was developed. The simulation studies were performed in Aspen Plus®. The effects of variables such as the reflux ratio, boil up ratio, feed flow rate and feed plate locations etc. are presented for RD column performance using sensitivity studies.
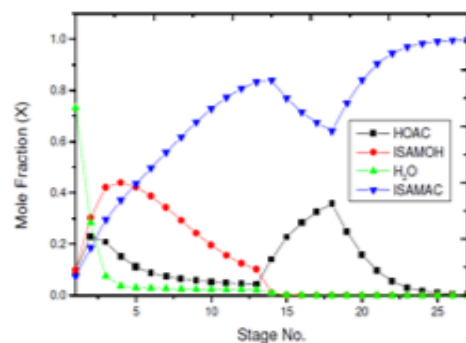

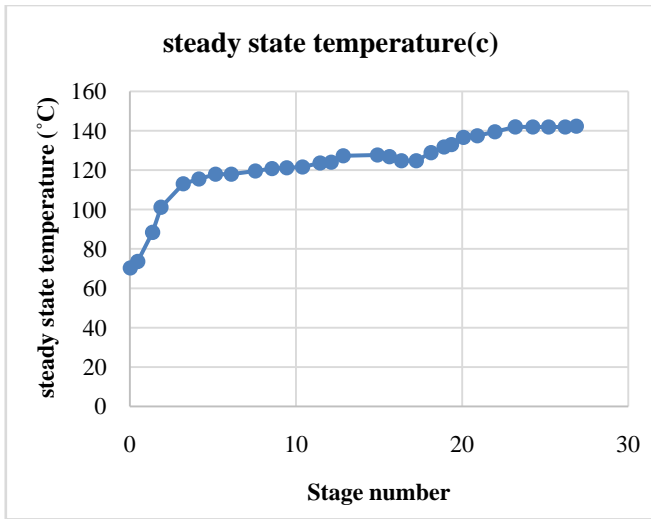**Fig. 3: Staedy state composition profile**

Fig. 4: steady state temperature profile

Fig. 5: Effect of boil up ratio on purity

Fig. 6: Effect of reflux ratio on purity

Fig. 7: Effect of feed stage location (iso amyl alcohol) on purity

Fig. 8: Effect of feed stage on purity

9. ACKNOWLEDGEMENTS

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NOMENCLATURE

ainterfacial area, m^2

B   bottoms flow, mol s^{-1}

c   number of components, dimensionless

C   molar conversion fraction of the reactant

D   distillate flow, mol s^{-1}

E   energy flux, W m^{-2}

F_vVapor feed stream, mol s^{-1}

F_LLiquid feed stream, mol s^{-1}

f   component feed stream, mol s^{-1}

h   heat transfer coefficient, W$m^{-2}K^{-1}$

H   molar enthalpy, J mol^{-1}

k_1Pseudo-first-order reaction rate constant, s^{-1}

K vapor-liquid equilibrium constant, dimensionless

L liquid flow rate, mol s^{-1}

M   molar holdup, mol

Q   heat duty, J s^{-1}

R   gas constant, m3 atm k$mol^{-1}sec^{-1}$

R   Reflux ratio

tTime, s

T   temperature, K

v   reaction volume (liquid holdup)

v_oVolumetric flow rate entering the stage

V   vapor flow rate, mol s^{-1}