



## Simulation and experimental studies on reactive distillation column for synthesis of Iso-amyl acetate

Kiran D. Patil<sup>1,\*</sup> and Bhaskar D. Kulkarni<sup>2</sup>

<sup>1</sup>Department of Petrochemical & Petroleum Engineering, Maharashtra Institute of Technology, Paud Road, Pune-411 038, India.

<sup>2</sup>Chemical Engineering & Process Development Division, National Chemical Laboratory, Homi Bhabha Road, Pune-411 008, India.

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### ABSTRACT

Reactive Distillation (RD) is the combination of chemical reaction and distillative product separation in single piece of equipment, offers a number of specific advantages over conventional sequential approach of reaction followed by distillation or other separation techniques. The experimental part includes RD experiments in laboratory scale, carefully evaluated database for describing chemical reaction and phase equilibria. The iso-amyl acetate synthesis is also carried out in a packed bed RD column operated in batch and continuous modes. This paper describes an investigation into experimental and simulation work of the heterogeneous esterification of acetic acid with iso-amyl alcohol, catalyzed by an acidic cation-exchange resin. The effects of the variables such as the reflux ratio, vapour rate and feed flow rate on iso-amyl acetate synthesis are studied experimentally. The simulations are based on the equilibrium-stage model approach. The simulation studies are performed in Aspen Plus and MATLAB. Finally results of sensitivity studies using Aspen plus are presented to show the optimum performance of RD column.

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### Introduction

The discipline of chemical engineering is undergoing a major transformation. A new paradigm of "*Borderless Chemical Engineering Science*" is emerging. The demands from the society for 'cleaner' technologies rather 'clean-up' technologies, the emergence of 'performance chemicals and materials' etc., is driving the profession towards achieving symbiotic relationship with other disciplines. The need for more efficient and environmentally 'cleaner' processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes. A drive towards 'Process Intensification' is leading to the search of novel reactor configurations, which will enhance selectivity as well as productivity [2]

The chemical and petroleum industries are experiencing fundamental changes. Rapid globalization of the industries, economic and political changes in the world order, environmentally driven governmental regulations and social pressures (e.g. decrease of consumption, increase of reuse and recycling), declining reserves of some raw materials, and increasing competition and overcapacity are the circumstances in which companies are fighting for their future existence. As a response, the chemical and petroleum industries are slowly realizing the significance of new technologies - compared to incremental improvements in the existing processes - as a means of producing products more competitively while simultaneously protecting the environment. The need for more efficient and environmentally 'cleaner' processes has led to a growing interest in novel processes and hybrid process systems, which combine conventional and non-conventional processes. [1, 2]

Reactive distillation (RD) for many different processes has been rapidly implemented in more than 150 commercial operations of the petrochemical and chemical industry. These

implementations show large capital and energy cost reductions, a lower environmental impact and safe and reliable operation. [1, 2] RD can also be seen as the front-runner in the field of process intensification. This combination can lead to intensified, high-efficiency process systems with remarkable green engineering attributes. [1] Green engineering (GE) principles have been described recently in the context of design, for manufacturing molecules in chemical processes and general products and systems. GE also have a major impact on byproduct formation as well as other factors identified in green engineering principles.[3] RD has been used as a "clean technology" for chemical synthesis in the industry because of advantages like saving of energy cost and capital cost.[4]

Combination of reaction and separation in a 'combo' system is likely to bring large dividends. RD is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over conventional sequential approach of reaction followed by distillation.[5] Enhancement in conversion, selectivity, energy utilization, reduction in equipment cost and separation of otherwise difficult to - separate mixtures are some of the motives behind its several applications. It has become an attractive technology not only for reaction engineers but also for separation technologists. [6]. Since RD involves interaction of reaction, distillation and mixing processes, its applicability for a particular reaction depends on the chemical and physical properties of the system and system components.[5,6]

These implementations show large capital and energy cost reductions, a lower environmental impact and safe and reliable operation.[1,2] Reliable scale-up from pilot plant facilities without intermediate demonstration scale seems to have been obtained in all cases. Academic research has led to methods

and tools to identify design and optimize new applications, however all for reversible reactions only. The present status seems to warrant the conclusion that reactive distillation is now an established unit operation in process technology. Reactive distillation can also be seen as the front-runner in the field of process intensification [1] The introduction of an *in situ* separation in the reaction zone or vice versa leads to complex interactions between vapour-liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products, reaction and distillation temperatures etc. and hence, the use of RD for every reaction may not be feasible. [3,6] However, there are feasibility constraints resulting both from thermodynamics and chemistry. In addition, the process intensification leads to higher complexity and thus the need for research in terms of model predictiveness and scale-up procedure. This holds especially true for the case of heterogeneously catalyzed reactive distillation with its complex interaction between vapours, liquid and immobilized solid catalyst phase. [4]

### Previous Studies

The recovery of dilute acetic acid from wastewater streams is a foremost dilemma in the petrochemical and chemical industries [7]. This includes the manufacture of cellulose esters, terphthalic acid, dimethyl terphthalate and reactions involving acetic anhydride. Acetic acid is commonly found in significant concentrations when one can make detailed characterization of industrial wastewater streams. The concentration of these acids can differ significantly. Among these processes, the process for the manufacture of cellulose acetate from acetylation of cellulose by acetic acid, acetic anhydride and sulfuric acid, is typically associated with a 35% w/w aqueous solution of acetic acid as a waste stream. Terphthalic acid process involves the concentration even up to 65% w/w if acetic acid in water [8]. The wood distillation contains much lower concentrations (1-8 % w/w) of acetic acid.

Saha et al. (2005) presented experimental studies on reactive distillation for esterification of iso-amyl alcohol with dilute acetic acid on laboratory RD column [7, 8].

In literature the kinetic studies for heterogeneous catalysed esterification of acetic acid with iso-amyl alcohol was reported. [7, 8, 9] Chiang et al., (2002) studied the two design alternatives for the Isoamyl acetate process, a coupled reactor column and reactive distillation. [9] The kinetic behavior of the heterogeneous esterification of acetic acid with amyl alcohol over an acidic cation-exchange resin, Dowex 50Wx8-100, was investigated by Lee et al, (2000) [10] Chiang et al, (2002) reported this process is four times more efficient than conventional process based on Total Annual Cost (TAC) [8]

In this work we have studied esterification reaction of acetic acid with iso-amyl alcohol in RD column, catalyzed by an acidic cation-exchange resin, TULSION, T-63.

### Esterification Reactions via Reactive Distillation

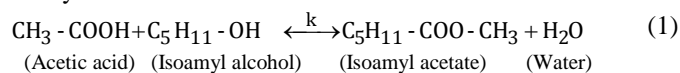
Esterification (e.g. synthesis of iso-amyl acetate/ n-hexyl acetate) has been the model reaction for the research studies in reactive distillation. Reaction of acetic acid with higher alcohols falls in a category of typical class of reacting systems. The alcohol is sparingly soluble in water and esters and water are almost immiscible. An additional feature is that the ester-water-alcohol forms a ternary heterogeneous azeotrope, which is minimum boiling. Hence, the vapours at the top condense to form two liquid phases of which aqueous phase is almost pure

water. One can conveniently separate water and enhance the conversion. [6,11]

The esterification of acetic acid with alcohols like *n*-butanol, ethanol, isobutyl alcohol, amyl alcohol and hexyl alcohol fall in a typical class of reacting systems.[6]

### Synthesis of iso-amyl acetate via RD

Iso-amyl acetate can be synthesized from acetic acid and Isoamyl alcohol via esterification reaction as follows:



**Table 1. Boiling points of the components [11]**

| Components      | Boiling points (°C) |
|-----------------|---------------------|
| Acetic Acid     | 118                 |
| Isoamyl Alcohol | 137.8               |
| Isoamyl acetate | 148.8               |
| Water           | 100                 |

Since the self-catalyzed reaction is rather slow, reaction (1) is commonly catalyzed using strong inorganic acid, like sulfuric acid, or strongly acidic ion exchange resins. Most of previous researcher used acidic cation exchange resin, for example Amberlyst-15 [3], Purolite CT- 175 [7, 8, 9]

The two reactants, acetic acid and iso-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 given in eq. (1) are well suited for reactive distillation. However, the large boiling temperature difference between the reactants can be unfavorable from the reactions point of view. [11]

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 Isoamyl acetate is produced during recovery of acetic acid by esterification with Isoamyl alcohol. An additional column will be required for the complete separation of iso-amyl alcohol and iso-amyl acetate. The column would not involve water since it has the highest latent heat and hence the energy costs would be minimized. [13]

Iso-amyl acetate has been used in the industry as a solvent, and extractants, and polishing agent. It is used as artificial flavoring in banana-flavored bubble gums, as preservative in sodas and soft drinks as well as artificial scent for covering unpleasant odors.[8] It is also used in large quantities in artificially pear- flavored food articles as additive in cigarettes, and as a solvent for tannins, nitrocellulose, lacquers, celluloid, and camphor. It is also used to manufacture celluloid cements, waterproof varnishes, artificial silk, leather or pearls, photographic films. [6,7,8]. iso-amyl acetate is also used to test the effectiveness of respirators or gas masks because it has a strong smell which is generally not experienced as unpleasant and that can be detected at low concentrations, and has low toxicity [7]

### 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. The equilibrium reaction is given by equation 1.[11, 16]

**Model Assumptions:**

The various assumptions made during the development of model were as follows:

- The vapour and liquid on each plate and leaving on each plate are perfectly mixed.
- Constant molar liquid hold-up is assumed for each stage.
- Molar vapour hold-up is negligible
- The liquid phase is in equilibrium with the vapour phase leaving the plate.
- The pressure decrease along the column height is assumed to be negligible.

The assumptions above lead to a model that consists of a set of ordinary differential and algebraic equations (DAE's). From the mass and energy dynamic balances on the  $j^{\text{th}}$  plate according to figure 1, the model is derived as follows[17]:

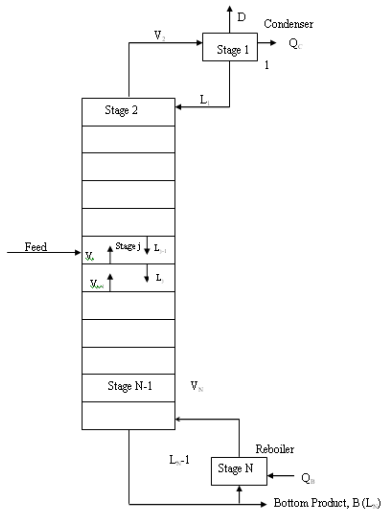


Figure 1. RD column for esterification reaction [11,17]

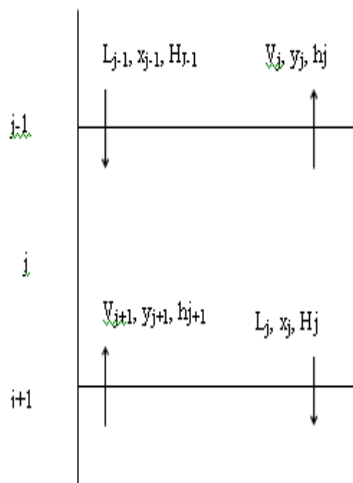


Figure 2. Single stage (j) in the column showing the corresponding streams [11,18]

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

$$\frac{d(x_{ij}M_j)}{dt} = V_{j+1}y_{ij+1} - L_jx_{ij} + L_{j-1}x_{ij-1} - V_jy_{ij} + \Delta R_{ij} \quad (2)$$

$$\frac{dx_{ij}}{dt} + M_j \frac{dM_j}{dt} x_{ij} = V_{j+1}y_{ij+1} - L_jx_{ij} + L_{j-1}x_{ij-1} - V_jy_{ij} + \Delta R_{ij} \quad (3)$$

This is combined with overall mass balance around plate  $J$ :

$$\frac{dM_j}{dt} = V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j \quad (4)$$

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:

$$y_{ij} = K_{ij}x_{ij} \quad (5)$$

where  $K$ = equilibrium constant

This gives following equation, which is as follows:

$$\frac{d(x_{ij})}{dt} M_j = V_{j+1}K_{ij} + 1x_{ij+1} - L_jx_{ij} + L_{j-1}x_{ij-1} - V_jK_{ij}x_{ij} + \Delta R_{ij} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j)x_{ij} \quad \dots (6)$$

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

$$\frac{d(H_{ij}M_j)}{dt} = V_{j+1}h_{ij+1} - L_jH_{ij} + L_{j-1}H_{ij-1} - V_jh_{ij} \quad (7)$$

$$\frac{dH_{ij}}{dt} M_j + \frac{dM_j}{dt} H_{ij} = V_{j+1}h_{ij+1} - L_jH_{ij} + L_{j-1}H_{ij-1} - V_jh_{ij} \quad (8)$$

This is combined with overall energy balance around plate  $J$ :

$$\frac{dH_{ij}}{dt} M_j = V_{j+1}h_{ij+1} - L_jH_{ij} + L_{j-1}H_{ij-1} - V_jh_{ij} - (V_{j+1} - L_j + L_{j-1} - V_j + \Delta R_j)H_{ij} \quad \dots (9)$$

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

**Phase Equilibria:**

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, iso-amyl alcohol, iso-amyl acetate, and water [1]. Vapor liquid equilibrium (VLE) data are available for all of the binary pairs, and liquid-liquid equilibrium (LLE) data for two ternary systems (acetic acid- iso amyl alcohol, water and acetic acid-iso-amyl acetate-water) [7, 9]

The reaction of iso-amyl alcohol and acetic acid forms a highly liquid phase azeotropes have been observed experimentally in the iso-amyl acetate system and other similar mixtures. [9] To account for nonideal vapor-liquid equilibrium (VLE) and possible vapor-liquid-liquid equilibrium (VLLE) for these quaternary systems, the NRTL (non random two liquid) model is used for activity coefficients. The NRTL equation is an activity coefficient model that correlates the activity coefficients  $\gamma_i$  of a compound  $i$  with its mole fractions  $x_i$  in the concerning liquid phase. The NRTL model predicts the presence of these azeotropes and was found to be accurate in estimating their compositions[17] A reasonable prediction of LL envelope can facilitate possible use of decanter which is often encountered in esterification reactive distillation systems. [9, 10] This is also the reason why the NRTL and UNIQUAC models are preferred for activity coefficients. [14] Since esterification reaction was carried out at atmospheric pressure, the vapor phase nonideality

considered is the dimerization of acetic acid as described by the Hayden-O'Connell second virial coefficient model. [10, 14]

The NRTL-model has been chosen for the description of the phase equilibrium data. Table 1 and 2 lists the model parameters for the present quaternary system where iso-amyl acetate system is described by the NRTL model. [9] The Azeotrope data for iso amyl acetate esterification system is given in Table 3.

#### Reaction Kinetics:

Reaction kinetics was developed and VLE data available in literature is used to predict the RD column performance and verify the model predictions. The kinetic expressions and other data is used for simulation work synthesis of Isoamyl acetate synthesis over cation-exchange resin (TULSION, T-63, Thermax India Ltd.)

$$r = (k_f C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_b C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}) \quad (10)$$

Lee et al (1999) reported the kinetic expressions for amyl acetate synthesis over Amberlyst 15 is used for simulation work [9]:

$$r = (k_f C_{CH_3COOH} \cdot C_{C_5H_{11}OH} - k_b C_{C_5H_{11}COOCH_3} \cdot C_{H_2O}) \quad (11)$$

$$k_f = 17500e^{-62232/T} \quad (12)$$

$$K_{eq} = \frac{k_f}{k_b} = 13.9e^{-777/T} \quad (13)$$

$$K_{eq} = 1.6 (T = 363K) \quad (14)$$

where  $m$  = mass of catalyst (kg)

Patil et al, (2010) reported the kinetic expression for iso-amyl acetate synthesis over ion exchange resin (T-63) is given by [11]:

$$k_1 = 3.54 \times 10^3 \exp\left(\frac{-41.88}{RT}\right) \quad (15)$$

#### Experimental Work:

##### Material and Catalysts

Acetic acid (99.8%) and is-amyl alcohol (99%) were purchased from Merck India Ltd., Mumbai. In the reactive zone structured packings, embedded with, cation ion exchange resin, T-63 (Thermax India Ltd.) was used as a catalyst. In stripping and rectifying sections (non-catalytic sections), HYFLUX structured packings were used. (High efficiency, low-pressure drop distillation packing) was used.[11]

The experimental set-up of a laboratory scale RD consists of 2.75 m tall distillation column of inside diameter 50 mm that operates at atmospheric pressure is used is as shown in figure 3. The reboiler (2 lit) is heated with the help of a heating coil provided in the reboiler. The non-reactive rectifying and stripping sections were packed with wire mesh packing.

##### Experimental Procedure

A laboratory RD experimental set up is designed and constructed to synthesize iso amyl acetate from iso amyl alcohol and acetic acid in order to support the simulation studies conducted via Aspen plus. The motivation and objectives for experimental investigations are to test the applicability of reactive distillation technology for iso-amyl acetate synthesis and validate steady state simulation results obtained from Aspen plus.

The experimental set-up of a laboratory scale RD consists of 2.5 m tall distillation column of inside diameter 50 mm that operates at atmospheric pressure is used is as shown in figure 3. The reboiler (2 lit) is heated with the help of a heating coil provided in the reboiler. The non-reactive rectifying and stripping sections were packed with wire mesh packing. The

middle reactive zone is packed with structured packing embedded with T- 63 MP as a catalyst. The stripping section is 1 m tall, reactive section 1 m, and rectification section 0.75 m tall in height respectively. A proper insulation (with asbestos) with external wall heating arrangement was provided to minimize the heat losses to the surrounding. The reaction mixture consisting of acetic acid, Isoamyl alcohol is fed continuously to the column through a feed module. Two separate peristaltic pumps (Range 1 -4 liters/hr.) were used to transfer the liquid from the two feed tanks to the two locations on the RD column.

In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, amyl alcohol and amyl acetate. Phase separator with the condenser is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Thermometer wells are provided at different locations in the column to measure these temperatures (Position 1- Position 7)

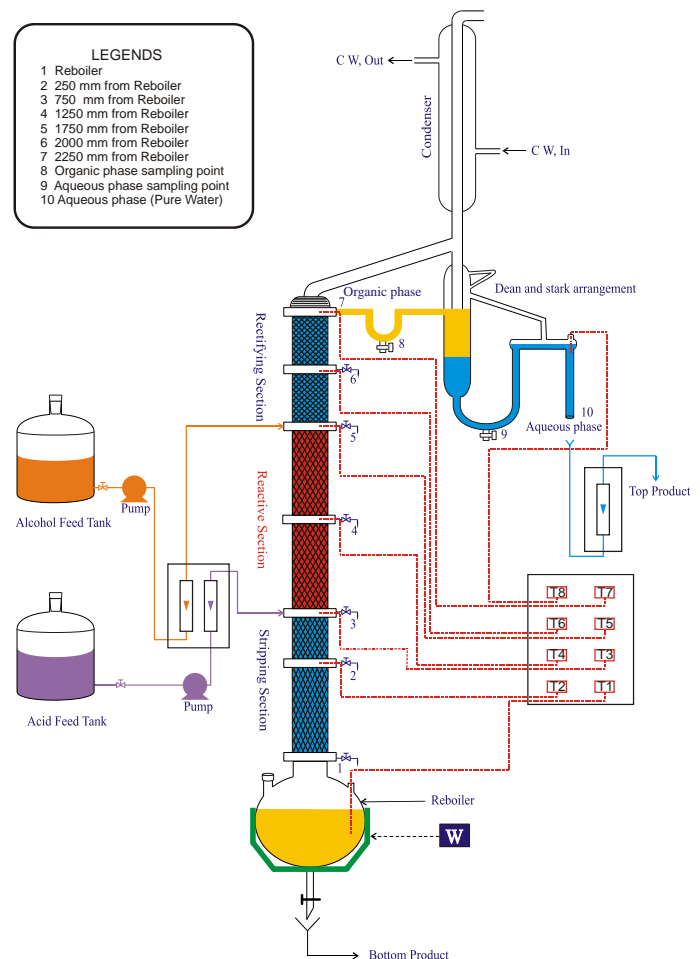


Figure 3. Experimental set up for Continuous RD Column[11]

#### Solutions of Model Equations

##### MATLAB Simulation

The model equations form a mixed set of set of ordinary differential equations (ODE's) and algebraic equations. The equations for 27 stages for the system and four-component system can be solved in MATLAB by ODE 15 S solver (which is an ordinary differential and algebraic equation (DAE) solver for stiff equations, variable order method) and using Aspen plus simulation[18]

**Table 2. Properties Catalyst used (Thermax Ltd., India) [12]**

| Catalyst | Particle size ( $\mu\text{m}$ ) | Exchange capacity (meqiv/dry g) | Bulk density ( $\text{kg/m}^3$ ) | Moisture content (%) | Porosity (%) | Temp stability (K) | Specific Surface area ( $\text{m}^2/\text{gm}$ ) | Pore Dia (A) | Cross linking (%) |
|----------|---------------------------------|---------------------------------|----------------------------------|----------------------|--------------|--------------------|--|--------------|-------------------|
| T-62     | 300-1200                        | 4.8                             | NA                               | <1                   | NA           | 403                | 35   | NA           | 15                |
| T-63     | 300-1200                        | 4.9                             | NA                               | <1                   | 40           | 403                | 35   | 400          | 15                |
| T-66     | 300-1200                        | 5.0                             | NA                               | <1                   | NA           | 403                | NA   | NA           | NA                |

**Table 3. Binary Parameters of the NRTL Model for Acetic acid (1) + iso-amyl alcohol (2) + iso amyl acetate (3) +Water (4) Systems [ 9 ]**

| $(j, i)$ | $A_{ij}(K)$ | $A_{ji}(K)$ | $\alpha_{ij}$ |
|----------|-------------|-------------|---------------|
| (1,2)    | -316.8      | 178.3       | 0.17          |
| (1,3)    | -37.94      | 214.6       | 0.2           |
| (1,4)    | -110.6      | 424         | 0.299         |
| (2,3)    | -144.8      | 320.7       | 0.301         |
| (2,4)    | 100.1       | 1448        | 0.298         |
| (3,4)    | 254.5       | 2222        | 0.2           |

**Table 4. Activity Coefficient Models Parameters for iso-amyl Acetate Esterification System [10]**

| Comp.i       | HOAC(1)   | HOAC(1)   | HOAC(1)             | ISAMOH(2) | ISAMOH(2)           | ISAMAC(3)           |
|--------------|-----------|-----------|---------------------|-----------|---------------------|---------------------|
| Comp.j       | ISAMOH(2) | ISAMAC(3) | H <sub>2</sub> O(4) | ISAMC(3)  | H <sub>2</sub> O(4) | H <sub>2</sub> O(4) |
| $b_{ij}$ (K) | -316.8    | -37.943   | -110.57             | -144.8    | 100.1               | 254.47              |
| $b_{ji}$ (K) | 178.3     | 214.55    | 424.018             | 320.6521  | 1447.1              | 2221.5              |
| $c_{ij}$     | 0.1695    | 0.2       | 0.2987              | 0.3009    | 0.298               | 0.2                 |

**Table 5. Azeotrope Data for iso amyl acetate Esterification System [9,10]**

| iso-amyl alcohol             | iso-amyl acetate         | iso-amyl alcohol         | Acetic acid                     | Acetic acid                |
|------------------------------|--------------------------|--------------------------|---------------------------------|----------------------------|
| iso-amyl acetate             | water                    | water                    | iso-amyl alcohol                | iso-amyl alcohol           |
| water                        | -                        | -                        | Iso-amyl acetate                | -                          |
| 94.71 <sup>0</sup> C         | 94.90 <sup>0</sup> C     | 95.80 <sup>0</sup> C     | <b>139.89<sup>0</sup>C</b>      | <b>140.07<sup>0</sup>C</b> |
| (0.0488, 0.1292, 0.822)      | (0.1696, 0.8304)         | (0.1512, 0.8488)         | <b>(0.2225, 0.6108, 0.1667)</b> | <b>(0.2585, 0.7415)</b>    |
| <b>94.9<sup>0</sup>C</b>     | <b>95.2<sup>0</sup>C</b> | <b>95.8<sup>0</sup>C</b> |                                 |                            |
| <b>(0.046, 0.107, 0.847)</b> | <b>(0.166, 0.834)</b>    | <b>(0.146, 0.854)</b>    |                                 |                            |

**Table 6. Reaction Kinetics Results [11]**

| Model | Pre-exponential factor (mols/g.min) | Activation energy (kJ/mol) | K <sub>1a</sub> | K <sub>2b</sub> | K <sub>3c</sub> | K <sub>4d</sub> | SRS                     |
|-------|-------------------------------------|----------------------------|-----------------|-----------------|-----------------|-----------------|-------------------------|
| LHHW  | 2.4 x 10 <sup>5</sup>               | 47                         | 0.23            | 2.12            | 0.34            | 2.12            | 2.37 x 10 <sup>-9</sup> |
| E-R   | 3.65 x 10 <sup>5</sup>              | 46.7                       | 0.99            | 6.10            | 2.41            | 8.97            | 4.35 x 10 <sup>-9</sup> |
| QH    | 3.39 x 10 <sup>3</sup>              | 40.3                       | -               | -               | -               | -               | 8.30 x 10 <sup>-9</sup> |
| PH    | 3.54x10 <sup>3</sup>                | 41.88                      | -               | -               | -               | -               | 6.75x10 <sup>-9</sup>   |

### Aspen Plus® Simulation

Aspen plus is a sequential modular simulation package, contains an extensive model library that allows most unit operations to be simulated easily and accurately. Despite the fact that a column equipped with structured packing, very good results were obtained using this model. Each unit operation block is solved in certain sequence. The process simulation capabilities of Aspen plus enables us to predict the behavior of a process using basic engineering relationships such as mass and energy balances, phase and chemical equilibrium, and reaction kinetics. With reliable thermodynamic data, realistic operating conditions and the rigorous Aspen plus equipment models, one can simulate actual plant behavior. Implementation of model equations and all simulations were carried out using the model RADFRAC from the steady-state simulator Aspen plus, which is based on a rigorous equilibrium-stage model for solving the MESH equations. [11, 17]

The model is both rigorous enough to represent the process complexity and simple enough to ensure the feasibility of the process simulation. Venkataraman, Chan and Boston (1990) describe the inside-out algorithm known as RADFRAC that is part of the commercial program Aspen plus. [16] Inside-out methods involve the introduction of new parameters into the model equations to be used as primary iteration variables. RADFRAC is able to handle both equilibrium reactions as well as kinetically limited reactions.

In built RADFRAC model for RD is used to simulate the equilibrium model in Aspen plus environment. The simulation is begun by putting together a basic flow sheet of a RADFRAC column with input streams of acetic acid and iso amyl alcohol and output streams on iso amyl acetate and water. The thermodynamic properties are calculated using the NRTL model The Hayden–O'Connell second virial coefficient model with association parameters was used to account for the dimerization of acetic acid in the vapor phase. [11] The Aspen Plus built-in association parameters are employed to compute fugacity coefficients. Such deviations are mainly caused by the dimerization of the acetic acid. A reaction rate for Pseudohomogenous model calculated by laboratory batch reactor is used for simulation to yield a steady state solution. [16]

### Results and Discussions:

The figure No. 4 and 5 shows typical composition profiles obtained by MATLAB and Aspen plus. The figure No. 6 (a) and (b) shows the comparison of temperature and composition profiles obtained by simulation using Aspen plus and our own experimental results conducted in Laboratory cum pilot scale RD column. It was observed that as boil-up increases, the amount of Isoamyl alcohol, which is excess in the feed, increases in top product thereby improving the purity of the bottom product. As anticipated, the time required to attain the steady state was more for lower boil-up rate.

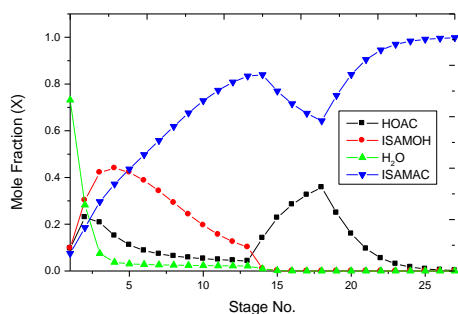


Figure 4. Steady State Composition Profiles (Aspen plus)

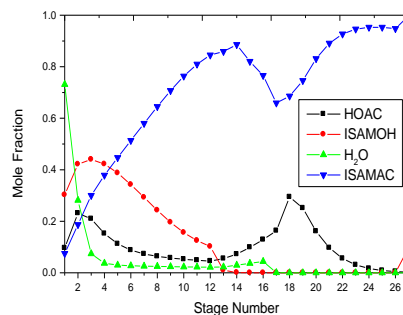
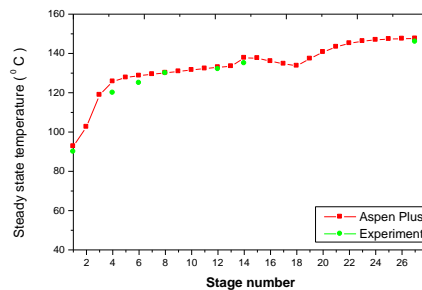
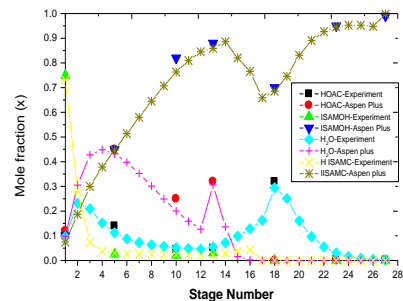


Figure 5 Steady State Composition Profiles ( MATLAB)



(a) Steady State Temperature Profile



b) Steady State Composition Profile

### Figure 6. Comparisons of Simulation and Experimental Results for Temperature and composition profiles

As can be seen from the simulation results as shown in figure 4 and 5, conversion of 99.5% of Isoamyl acetate, with Isoamyl acetate purities of 88.4 % was achieved. The extremely low concentration of water in the reactive zone helps reaction to proceed near completion. The composition at position 7 comprises of two phases viz. organic and aqueous phase. In all the runs, the temperature in reactive zone is in the range of 120-130°C. Sufficiently high temperature ensure reaction to be at the chemical equilibrium and driven by distillation. The temperature is below the limit set by the thermal stability of the catalyst (135 °C) (T-63, Thermax Ltd., India). [9] Figure 6 shows the comparison of simulation and experimental runs for typical run on RD column. This validated model is used to study the effect of various parameters for RD column performance using sensitivity studies.

### Sensitivity Studies:

Figure 7 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 figure 8 it is clear that as we increase the reflux ratio, the top product purity also increases, following linear relation. Figure 9 and 10 depicts effect of feed plate location on top product purity. It was observed that feed stage 13 for acetic acid and feed stage 18 from Isoamyl alcohol is the best-feed locations for these two reactants.

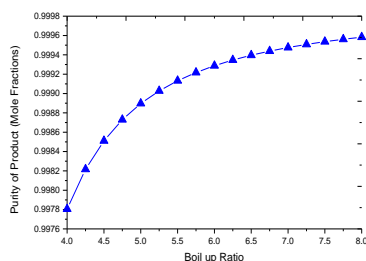


Figure 7. Effect of Boil up Ratio on Purity

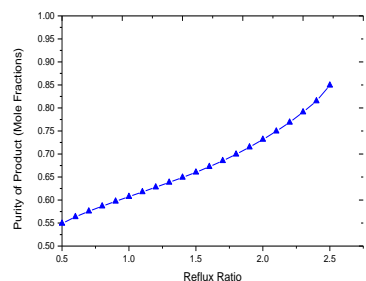


Figure 8. Effect of Reflux Ratio on Purity

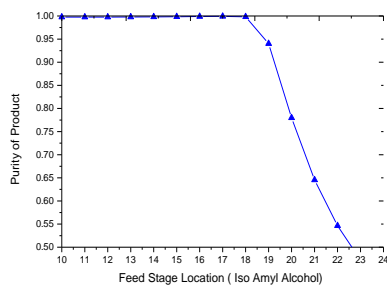


Figure 9. Effect of Feed Stage Location (Isoamyl Alcohol) on purity

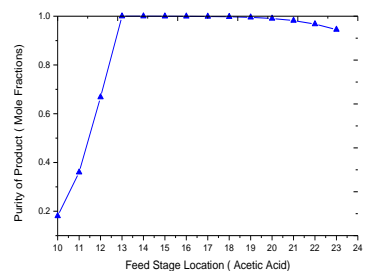


Figure 10. Effect of Feed Stage Location (Acetic Acid) on purity

## Conclusion

The equilibrium model for synthesis of Isoamyl acetate was developed. The simulation studies were performed in Aspen Plus and MATLAB. The experiments were carried out for the synthesis of Isoamyl acetate using laboratory cum pilot scale reactive distillation column to study the influence of various operating parameters such as a feed flow rate, feed compositions, boil-up rate etc. on the conversion and separation. The published experimental data on phase equilibrium and reaction studies was used to verify the model predictions. The experimental results from RD experiment in our laboratory were compared with model predictions and were found to be close to those available in literature.

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## Nomenclature

### Notations:

|           |   |
|-----------|---|
| c         | number of components, dimensionless                                     |
| C         | molar conversion fraction of the reactant                               |
| E         | energy flux, $W m^{-2}$   |
| $F^V$     | vapour feed stream, $mol s^{-1}$  |
| $F^L$     | liquid feed stream, $mol s^{-1}$  |
| f         | component feed stream, $mol s^{-1}$                                     |
| h         | heat transfer coefficient, $W m^{-2} K^{-1}$                            |
| H         | molar enthalpy, $J mol^{-1}$  |
| $k_1$     | pseudo-first-order reaction rate constant, $s^{-1}$                     |
| K         | vapor-liquid equilibrium constant, dimensionless                        |
| L         | liquid flow rate, $mol s^{-1}$  |
| M         | molar hold-up, mol  |
| Q         | heat duty, $J s^{-1}$   |
| r         | number of reactions, dimensionless                                      |
| $r_j$     | ratio of side stream flow to inter stage flow on stage j, dimensionless |
| $R_{m,j}$ | reaction rate, $mol m^{-3} s^{-1}$                                      |
| R         | reflux ratio  |
| t         | time, s   |
| T         | temperature, K  |
| v         | reaction volume (liquid hold-up)  |
| $v_o$     | volumetric flow rate entering the stage                                 |
| V         | vapour flow rate, $mol s^{-1}$  |
| x         | mole fraction in liquid phase, dimensionless                            |
| y         | mole fraction in vapour phase, dimensionless                            |
| HOAC      | acetic acid   |
| ISAMOH    | iso-amyl alcohol  |
| ISAMAC    | iso-amyl acetate  |

### Subscripts

|   |                              |
|---|------------------------------|
| i | component index              |
| I | referring to interface       |
| j | stage index                  |
| t | total                        |
| D | distillate                   |
| n | stage                        |
| k | base component (Acetic Acid) |

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