Continuous Reactive Distillation

Objective:
Perform the simulations of continuous reactive distillation using ASPEN PLUS simulator and compare the simulation results with experimental data for a given reaction system.

Reactive distillation
Reactive Distillation (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 or other separation techniques. Improved selectivity, increased conversion, better heat control, effective utilization of reaction heat, scope for difficult separations and the avoidance of azeotropes are a few of the advantages that are offered by RD. The introduction of an in situ separation process in the reaction zone or vice versa leads to complex interactions between vapor–liquid equilibrium, mass transfer rates, diffusion and chemical kinetics, which poses a great challenge for design and synthesis of these systems. RD being a relatively new field, research on various aspects such as modeling and simulation, process synthesis, column hardware design, non-linear dynamics and control is in progress. The suitability of RD for a particular reaction depends on various factors such as volatilities of reactants and products along with the feasible reaction and distillation temperature. Hence, the use of RD for every reaction may not be feasible. Exploring the candidate reactions for RD, itself is an area that needs considerable attention to expand the domain of RD processes. Although invented in 1921, the industrial application of reactive distillation did not take place before the 1980’s.

The esterification of acetic acid with alcohols like n-butanol, ethanol, isobutyl alcohol and amyl alcohol fall in a typical class of reacting systems. Butyl acetate is an industrially important chemical with wide applications as a versatile solvent. n-Butyl acetate is manufactured by the esterification of acetic acid with n-butanol in the presence of suitable acid catalyst. The alcohol is sparingly soluble in water and the ester is almost insoluble. Another interesting feature of this system is that it is associated with the
formation a minimum boiling ternary azeotrope of ester, alcohol and water, which is heterogeneous in nature. Hence, in a typical reactive distillation column that consists of both reactive and non-reactive zones, the heterogeneous azeotrope or a composition close to the azeotrope can be obtained as the distillate product. Moreover, the aqueous phase that forms after the condensation of the vapor is almost pure water. Depending on the requirement either of the phases can be withdrawn as a product and the other phase can be recycled back as reflux. The pure ester i.e. butyl acetate is the least volatile component in the system is realized as a bottom product.

In reactive distillation scheme, the option of using a conventional reactor for partial reaction followed by a reactive distillation column has been reported to have offered better economics. The simulation studies on the butyl acetate synthesis have also indicated that this option can be better than conducting the entire reaction in a reactive distillation column. The present work is aimed at performing a detailed experimental investigation on a reactive distillation column operated in such a mode.

Experimental

Material and catalysts
The packing used in the reactive distillation column were KATAPAK-S embedded with Amberlyst-15 catalyst and non-catalytic HYFLUX high efficiency low pressure drop wire mesh distillation packing.

KATAPAK-S
KATAPAK-S (S implies Sandwich) is a structured catalyst support for use in gas–liquid reaction systems such as trickle bed reactors, bubble columns or reactive distillation processes, in which catalyst granules can be embedded Fig. 1 (a). It is suitable for many catalytic applications, such as esterifications, etherification, and hydrogenations reaction. KATAPAK-S is immobilized between two sheets of metal wire gauze, forming “sandwiches”. Each of these sheets is corrugated, resulting in a structure with flow
channels of a defined angle and hydraulic diameter. The sandwiches are assembled with the flow channels in opposed orientation, so that the resulting unit is characterized by an open cross-flow structure pattern. The sandwich exists of 16 triangular channels, with a total of 32 cross-overs. A single triangular channel has a base of 36 mm, and a height of 18 mm. There is a 2 mm gap between the bases of adjoining triangular channels Fig. 1 (b). Inside such a sandwich, catalyst particles are present; the liquid flows inside these packed channels. When taking two of these sandwiches and placing them together, the space in between the two sandwiches is geometrically nearly equal to the inside of a packed channel. The channels that will be formed by this space are referred to as the open channels; no catalyst particles are present in the open channels. The gas flows through these open channels.

![Figure 1 (a) KATAPAK-S Structure](image)
Figure. 1 (b) Reconstruction of KATAPAK-S, a set of intersecting triangular tubes

HYFLUX

HYFLUX is structured tower packings made of stainless steel 304 and 316, are particularly useful when a moderate to large number of theoretical stages have to be accomodated in a limited height of the tower. HYFLUX is manufactured from a multitude of fine metallic wires which are knitted into a tube which is flattened, crimped, plied and custom formed to meet exacting specifications Fig. 2.

Figure 2 HYFLUX noncatalytic Packing
The open structure formed due to the proprietary lay of the filaments, the unique stitches employed and the special crimping and plying form tortuous channels for liquids which can continuously combine, divide and recombine for optimum mixing and contact with vapour. This results in intimate mixing between vapour passing upward through the controlled interconnecting passageways and the thin film of liquid flowing down the capillary wire network of the packing. The unique interaction results in high mass transfer rates (maximum separation efficiency) while maintaining low resistance to flow (low AP / theoretical stage).

**Specifications**

<table>
<thead>
<tr>
<th>HETP</th>
<th>≥ 100 to 200 mm in production columns</th>
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<tbody>
<tr>
<td>≥ 75 mm</td>
<td>in pilot/laboratory stills</td>
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<tr>
<td>NTU/metre</td>
<td>≤ 10 in production columns</td>
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<tr>
<td>≤ 13</td>
<td>in pilot/laboratory stills</td>
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<tr>
<td>ΔP / theoretical plate</td>
<td>0.05 - 0.75 mm Hg</td>
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<tr>
<td>Vapour load</td>
<td>0.2 - 2.75 F factor [m/s √kg/M3]</td>
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<tr>
<td>Liquid load</td>
<td>&lt;0.7 m 3 /m 2 h</td>
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<tr>
<td>Liquid holdup</td>
<td>3 to 8% w/w</td>
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</table>

**Apparatus and procedure**

The experimental setup of a laboratory scale reactive distillation plant is as shown in Figure 3. A 3m tall distillation column of inside diameter 54 mm that operates at atmospheric pressure was used. The reboiler (3 lit) was externally heated with the help of a heating mantle. The non-reactive rectifying and stripping sections were packed with Evergreen HYFLUX packing made out of fine metallic wires. The middle reactive zone was packed with Sulzer KATAPAK-S packing embedded with ion exchange resins Amberlyst-15 as a catalyst. All the sections are 1m tall in height. A proper insulation with external wall heating arrangement was provided to minimize the heat losses to the surrounding. The reaction mixture consisting of acetic acid, butanol, butyl acetate and water or an equilibrium mixture from the batch reactor is fed continuously to the column through a rotameter. An electronically driven metering pump is used to transfer the liquid from the feed tank to the column. In the condenser, two immiscible phases are formed, an aqueous phase i.e. almost pure water and an organic phase containing water, butanol and butyl acetate. The feed is preheated before introducing it to the column. Phase separator
with the condenser is used to provide reflux to the column and to continuously withdraw water formed during the reaction. Temperature sensors Pt 100 are provided at different locations in the column to measure these temperatures (Position 1- Position 8).

**Analysis**

The samples were analyzed using Gas Chromatograph (GC, C-911, Mak Analytica India Ltd.) equipped with thermal conductivity detector (TCD). The column used for the analysis was porapack–Q with hydrogen as carrier gas at the flow rate of 20 ml/min. Injector and detector were maintained at 220 °C and 150 °C respectively. The oven temperature was maintained isothermally at 240 °C to get best resolution in less time. The results obtained by GC were confirmed by independent titrations using standard sodium hydroxide solution. The samples were also analyzed by titrating them against NaOH using phenolphthelin as indicator.
Fig 3 Experimental set up of continuous reactive distillation

Observations:
<table>
<thead>
<tr>
<th>S.N.</th>
<th>Measurements</th>
<th>Values</th>
<th>Units</th>
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<tbody>
<tr>
<td>1</td>
<td>Feed Flow Rate</td>
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<tr>
<td>2</td>
<td>Top Flow Rate</td>
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<tr>
<td>3</td>
<td>Bottom Flow Rate</td>
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<tr>
<td>4</td>
<td>Feed Composition</td>
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<tr>
<td>5</td>
<td>Conversion</td>
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<tr>
<td>6</td>
<td>Purity</td>
<td></td>
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<tr>
<td>7</td>
<td>Reboiler Duty</td>
<td></td>
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<tr>
<td>8</td>
<td>Strength of NaOH Solution</td>
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</table>

**Steady State Column Profile:**

<table>
<thead>
<tr>
<th>Stage</th>
<th>Wall Temperature</th>
<th>Column Temperature</th>
<th>Titer value</th>
<th>Acetic Acid Concentration</th>
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<tbody>
<tr>
<td>1</td>
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Simulation of Continuous Reactive Distillation column with AspenPlus

Continuous reactive distillation column simulations for a given reaction can be carried out using RADFRAC steady state model in aspen plus. The effect of different operating conditions and different parameters can also be checked. A brief introduction on various problems/error messages encountered during simulation is given at the end.

Base case:

*Feed specification:*

1. Molar flow rates:
   - Feed 1 .......... mol/s
   - Feed 2 .......... mol/sec
2. Temperature:
   - Feed 1 320 K
3. Pressure 1 atm
4. Composition of feed
   - Feed 1 ..........
   - Feed 2 ..........

*Column specifications/operating Conditions*

1. Number of stages 21
2. Rectifying section 2-8
3. Reactive section 9-12
4. Stripping section 13-21
5. Amount of catalyst 0.015 (kg of catalyst/stage)
6. Reflux ratio ..........
7. Bottom flow rate ........ (mol/sec)
The chemical reaction considered is:

\[ A + B \leftrightarrow C + D \]

The forward and backward rate of reaction is formulated in terms of mole fraction. The forward rate of reaction is given by:

\[ \text{Ask for the data} \]

The corresponding backward rate is given by:

\[ \text{Ask for the data} \]

The UNIQUAC equation can be used to estimate the liquid phase non-idealities and vapor phase may be assumed to be ideal. The initial guesses to be provided to the Aspen Plus may be discussed with the instructor.

Results: Students are expected to submit the simulation results for the system used in their UG lab experiment.

Also answer the following questions and present simulation results, if applicable.
What happens if change following parameters/models

1. feed flow rate?
2. operating pressure?
3. reboiler duty?
4. catalyst loading?
5. thermodynamic model?
6. reflux ratio?
7. feed location?
8. Any other parameter?

Justify your results
Problems encountered during simulation in Aspenplus

(1) Fatal error
Fatal error generally occurs may be because of the following reasons
   (i) Fatal error mainly occurs due to lack of disk space
   (ii) Fatal error mainly occurs due to some server problem
   (iii) May be due to some severe errors in simulation

(2) Severe error
Severe error indicate that a serious error has been detected that will make continued execution unlikely, or will cause further error, terminal errors or incorrect results to occur.
There are so many reasons due to which severe error can occur, some of them are
   (i) Due to some conflict statements in your simulation
   (ii) Due to material/energy imbalance
   (iii) Due to column dry up

(3) Error messages with results
Error indicate that an error has been detected and that the system has been taken action that may correct the problem; execution continues but further errors, severe errors, terminal errors or incorrect results may occurs.
Error messages occurs because of
   (i) Your converged error is greater then tolerance limit
   (ii) Due to initial estimates
   (iii) insufficient number of iterations

(4) Warning with results
Warning indicates that a condition has been encountered, the system has taken action that is probably correct, and execution will probably continue normally.
Warning with results occurs when you exceed specified upper and lower limit of any given parameter.