Studies in Continuous Reactive Distillation:

Esterification Reaction for the synthesis of Butyl acetate

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Abstract: The esterification of acetic acid with n-butanol was studied in the presence of ion-exchange resin catalysts such as Amberlyst-15 to determine the intrinsic reaction kinetics. The effect of various parameters such as temperature, mole ratio, catalyst loading, and particle size was studied. Kinetic modeling was performed to obtain the parameters related to intrinsic kinetics. Pseudohomogeneous model was developed The rate expressions would be useful in the simulation studies for reactive distillation. The experimental data generated for the reaction under total reflux were validated successfully using the developed rate equation and estimated values of kinetic parameters.In this work, the synthesis of butyl acetate, starting from n-Butanol and acetic acid, using reactive distillation on acidic polymeric resins is investigated. The study proceeds to the continuous process to achieve the steady state equilibrium of the involved multi component mixtures and then to the study modifications to be done for the achievement of the maximum   seperation. Next, the separation-reaction process is investigated using a continuous Reactive distillation .(Gangadwala, J.; Mankar, S.; Mahajani, S.,2003)

Keywords: Reactive distillation, equilibrium, pseudohomogneous.

Introduction:

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. Reactive distillation provides an attractive alternative for process intensification, especially for reaction/separation systems with reversible reactions. 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. The important limitation of the Rd is that the volatilities of the components should be favorable. In the present system if we want to remove water, it should either have highest volatility or it should form minimum boiling azeotrope (constant boiling mixture) with one or more than one components in the system.

Components	Boiling points (^0C)
AcAc	118
n-BuOH	117.7
n-BA	126.3
Water	100

Table 1: Boiling points of the components

If we want to increase the conversion towards the butyl acetate, we have to remove water efficiently during the course of reaction. The boiling points in table 1 may indicate that water and other components have close boiling points and the efficient removal of water may not be possible, as water will possibly carry other components along with it in the overhead product. Water forms ternary azeotrope with BuOH and BA that boils at 87-90 ^0C. since this azeotrope is a minimum boiling azeotrope, instead of pure water one gets distillate composition close to the ternary azeotrope. The azeotrope can be either homogeneous or heterogeneous. If on condensation of the vapors, the liquid forms two phases, the azeotrope is called heterogeneous azeotrope. In the present system, the azeotrope is heterogeneous and forms two liquid phases on condensation. The aqueous phase is almost pure water and organic phase that consists of mainly BA and BuOH can be recycled back to the column through reflux. Hence, ideally in the batch RD mode if one starts with stoichiometric ratio of BuOH and AcAc in the reactor, at the end of the experiment, the system should contain only BA in the reactor, if losses of BuOH and other components with the overhead aqueous phase are negligible.Reactive Distillation is an attractive method for chemical synthesis because chemical reactions and product separation occur simultaneously in the same unit. For esterification reactions it is the most effective method of synthesis.

Experimental work
Material and catalysts

n-Butanol and acetic acid bith AR grade as well as commercial grade were obtained from S. D. Fine Chemicals Ltd., India. The packing used in the reactive distillation column were sulzer KATAPAK-S (catalytic packing) 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. 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.
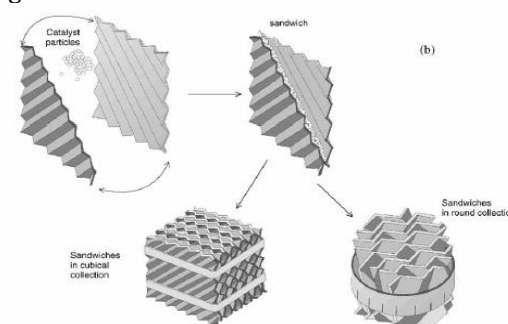

Figure 1:KATAPAK-S Structure

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.

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
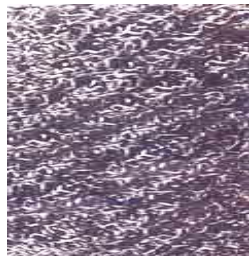

Figure 2: HYFLUX wire mesh Packing

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).

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).For the tall columns the convectional losses from the column wall to the environment are significant. Hence the column wall temperature is maintained at slightly higher temperature to reduce these losses. A wall heater is provided for this purpose and the outside wall temperature at several locations along the column height is measured through a multi channel temperature indicator.(Hiwale et al, 2002)

The column consists of following different zones:-

a) **Reactive zone**:- This is a middle section packed with catalytic packing, KATAPACK-S, which plays a dual role. It acts as catalyst and it also provides sufficient interfacial area for gas-liquid mass transfer. The reaction of AcAc and butanol takes place in this section and the products formed undergo distillation.

b) **Non-reactive rectifying zone**:- this is a top sectin that seperates the minimum boiling azeotrope of the ternary mixture butanol, butyl acetate and water (B.P. 87-90 ^{0}C) from the other components.

c) **Non-reactive stripping section**:- this is a bottom section used for the separation of the highest boiling butyl acetate from the other components.

Batch operation procedure: Firstly the column was operated under total reflux conditions for 30 min. Then the valve of the top product line was opened. During batch reactive distillation, top product flow rates were measured periodically (every after 60 min). Samples from the top product were taken every 60 min. The batch operation conditions, initial mole ratios, reflux ratio

Continuous operation procedure: The column was operated under total reflux conditions for 30 min. Then the feed and bottom product pumps were turned on and the valve of the top product line was opened. During continuous reactive distillation, top and bottom product flow rates were periodically measured every 60 min. Samples from the top product for GC analysis were also taken every 60 min. The steady state was achieved within 5-6 hours.
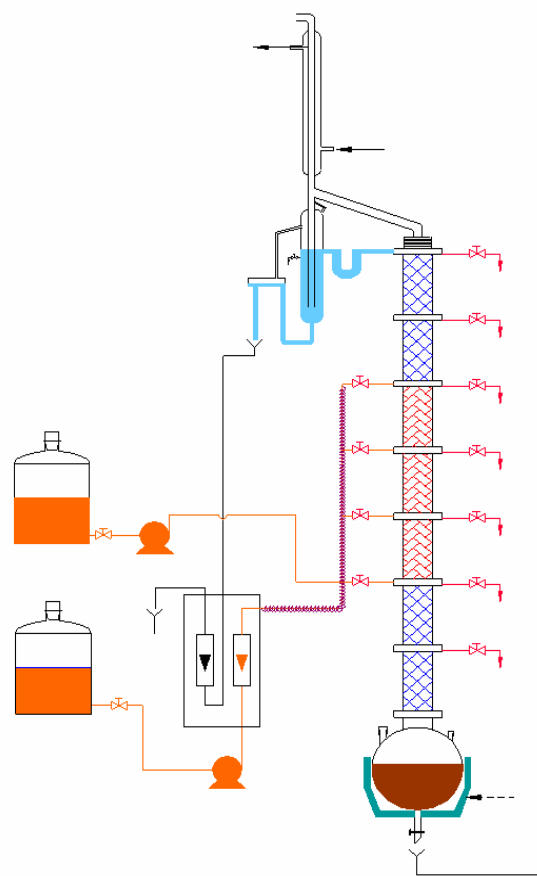
Figure 3: Schematic diagram for the reactive distillation set up

Analysis

The samples were analyzed using Gas Chromatograph (GC, C-911, MakAnalytica 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 ^{0}C and 150 ^{0}C respectively. The oven temperature was maintained isothermally at 240 ^{0}C to get best resolution in less time.

Practical design considerations:

Towler and Frey (2000) have highlighted some of the practical issues in implementing a large scale RD application. These are discussed below:

a) Installation and containment and removal of the catalyst: It is important to allow easy installation and removal of the RD equipment and catalyst. If the catalyst undergoes deactivation, the regeneration is most conveniently done ex situ

and so there must be provision for easy removal and installation of catalyst particles.

b) Good liquid distribution and avoidance of channeling: Liquid maldistribution can be expected to have more severe effect in RD than in conventional distillation. Good radial dispersion through the catalyst bed. This is required in order to avoid reactor hotspots and runaways and allow even catalyst ageing. The requirement of good radial mixing has an impact on the choice of the packing configuration and geometry.

c) Good vapor/liquid contacting in the reactive zone: If the reaction rate is fast and the reaction is equilibrium limited then the required size of the reactive zone is strongly influenced by the effectiveness of the vapor liquid contacting. Vapor/liquid contacting becomes less important for slower reactions. Commonly used devices for good vapor/liquid contacting are the same as for conventional distillation are include structured packing, random packing and distillation tray.

d) Low pressure drop through the catalytically packed reactive section: This problem arises because of the need to use small catalyst particles in the 1-3 mm range in order to avoid intra particle diffusion limitations. Counter current operation in catalyst beds packed with such small sized particles had to be specially configured in order to avoid problems of excessive pressure drop and flooding.

e) Sufficient liquid hold up in the reactive section: The liquid hold up, mean residence time and liquid residence time distribution are all important in determining the conversion and selectivity of RD. This is in sharp contrast with conventional distillation where liquid hold up and RTD are often irrelevant as the vapor liquid mass transfer is usually controlled by the vapor side resistance.

f) Designing for catalyst deactivation: It is desirable to allow on line catalyst removal regeneration. Such device has not been commercialized as yet. Catalyst deactivation is there fore accounted for in the design stage by use of excess catalyst. Besides adding excess catalyst, the reaction severity can be increased by (i) increasing reflux, leading to increase residence time and (ii) increasing reaction temperature (by increase of column pressure).

RESULTS AND DISCUSSIONS

In the first stage of experiments were carried out for the synthesis of butyl acetate on the existing pilot scale RD set up. In this section, runs on the main RD configuration had been studied. We studied the effects of different operation parameters such as reboiler duty, catalyst loading and feed composition. After collecting the experimental data for the different conditions, we selected the optimized condition, in order to study the time required for the attainment of steady state, a single run was conducted for 52 hours continuously. The feed flow rate was maintained at 0.634 lit/hr. It was observed that minimum 22 hours are required to obtain the steady state. The feed composition for 52 and 22 hrs run as shown in table.

Component	Mole fraction (Run-1)	Mole fraction (Run-2)
Acetic acid	0.177	0.177
Butanol	0.229	0.189
Water	0.261	0.273
Butyl acetate	0.333	0.361

Table 2 : Feed composition (22 hrs and 52 hrs run)

Effect of reboiler duty:

Figure shows the change in the BA and DBE composition in the bottom with changing reboiler heat duty for the feed composition (case-1). It can be seen that the reboiler heat duty above 0.4 kJ/hr gives BA purity above 96%, also shows that increase in heat duty DBE in bottoms increases. This may be due to the increase in the residence time, which has in turn produces more side product. Further simulation runs can be carried out to find the optimized value for heat duty.
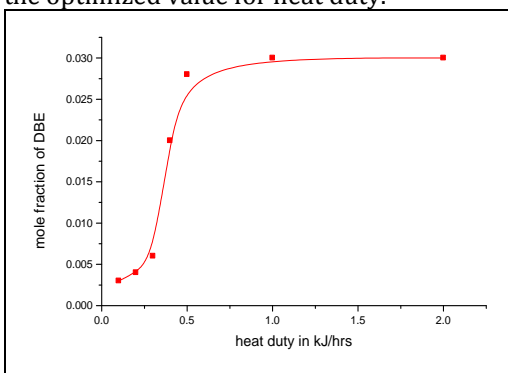

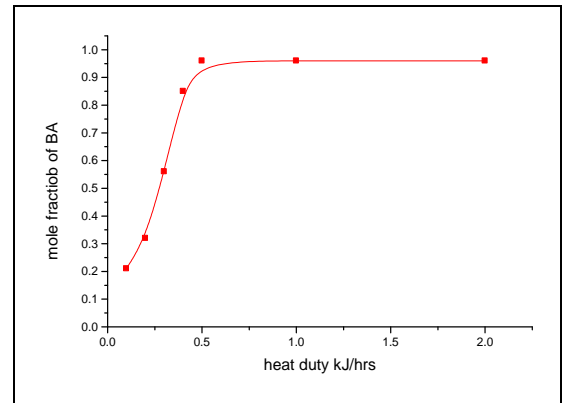**Figure** 4: Effect of reboiler heat duty on mole fraction of DBE in bottoms

Figure 5: Effect of reboiler heat duty on mole fraction of BA in bottoms

Effect of catalyst loading:

As expected, it has been found that increasing the catalyst loading helps to improve the production of BA to some extent, but at high loadings side reaction favored. Interestingly at high loading AcH composition found to be increasing. The water produced from the reaction may have reacted off some of the butyl acetate in the reverse direction to five BuOH and AcH.
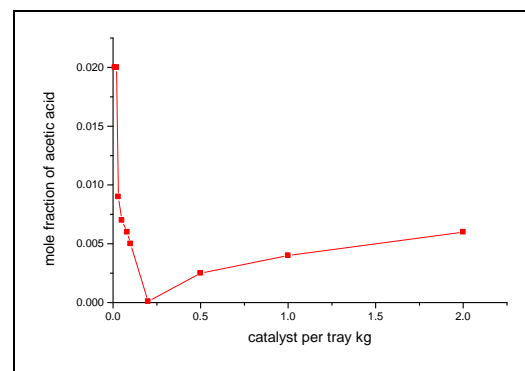

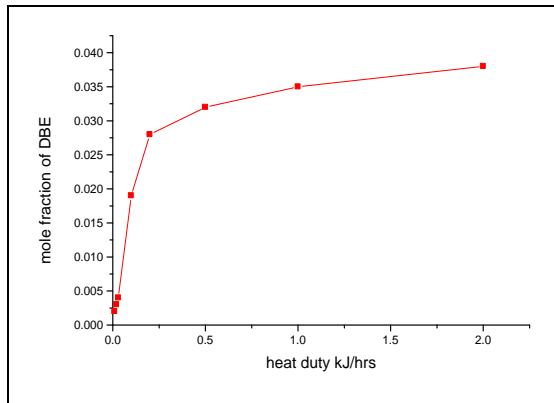**Figure 6:** Effect of catalyst loading on mole fraction of acid in the bottoms

Figure 7: Effect of catalyst loading on mole fraction of DBE in the bottoms

Effect of feed composition:

The excess butanol in the feed leads to formation of side product dibutyl ether, which is undesired. CRD with feed composition 1:1.3 mole ratio of acid to butanol (run-1) showed significant ether formation at steady state (1 mole% in bottom). In this case the concentration of butanol and water were quite high in reactive section whereas acetic acid concentration was quite low. Changing feed composition to 1:1.07 mole ratio of acid to alcohol (run-2), at steady state, drastic reduction in ether formation was noticed. At steady state, composition profile inside column showed high concentration of acid (more than run-1) and water (less than run-1) in the reaction zone and less concentration of butanol compared to case-1. Therefore, providing higher mole ratio of acid in feed to the column, ether formation can be suppressed significantly.

Effect of feed tray location:

As the feed tray location is shifted down from top to bottom, the BA concentration gradually decreases in the bottoms. The reactants such as butanol and acid increases gradually in the bottoms as the feed tray location shifted downwards. This part has been a part of future work, to investigate the effect of feed tray locations from F1 to F6.

Study of performance of Reactive distillation column:

The steady state concentration profiles are shown in figures 8 and 9 for 22 hrs and 52 hrs respectively. It was observed that acetic acid and n-butanol are almost negligible in the bottom of the RD. Thus almost pure butyl acetate is obtained at the bottom of the RD. The conversion obtained close to 100%. Interestingly, the bottom stream contains butyl acetate free of acetic acid. The excess butanol in the feed leads to formation of side

product dibutyl ether, which is undesired. CRD with feed composition 1:1.3 mole ratio of acid to butanol (Run-1) showed significant ether formation at steady state (1 mole% in bottom). In this case the concentration of butanol and water were quite high in reactive section whereas acetic acid concentration was quite low. Changing feed composition to 1:1.07 mole ratio of acid to alcohol (Run-2), at steady state, drastic reduction in ether formation was noticed. At steady state, composition profile inside column showed high concentration of acid (more than run-1) and water (less than run-1) in the reaction zone and less concentration of butanol compared to run-1. Therefore, providing higher mole ratio of acid in feed to the column, ether formation can be suppressed significantly.The conversion in reactive distillation is higher than that in conventional steady state reactor. Thus, the use of reactive distillation for this system is justified. The improvement is observed not only through the enhancement in the rate and hence the reduced reactor volume but also through the partial separation of the components involved, thereby reducing the capital and energy cost of downstream processing.
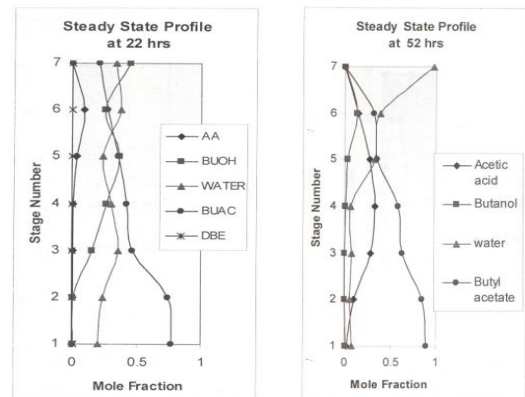

Figure 8:: Concentration profile obtained from pilot plant reactive distillation column (22 hrs and 52 hrs)
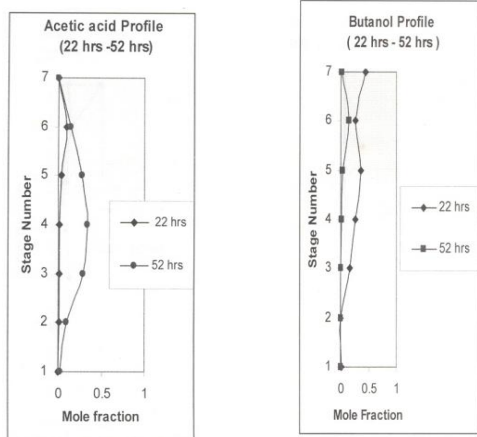
Figure 9: Comparison of Individual concentration profiles (22 hrs and 52 hrs)   (for Acetic acid and Butanol)
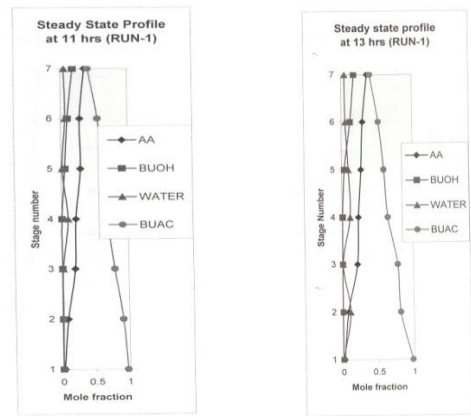

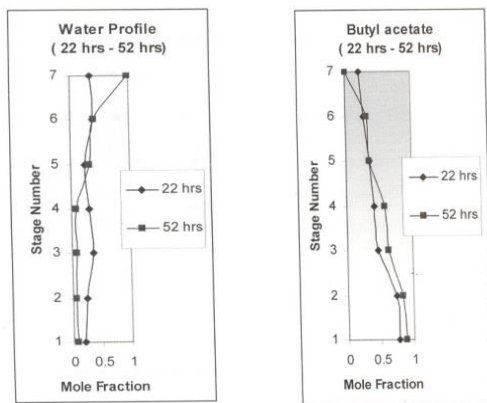**Figure 12:** Concentration profile obtained through reactive distillation column (Run -1) (9, 10 hrs)

Figure 10: Comparison of individual concentration profiles (22 hrs and 52 hrs)   (for Water and Acetic acid)
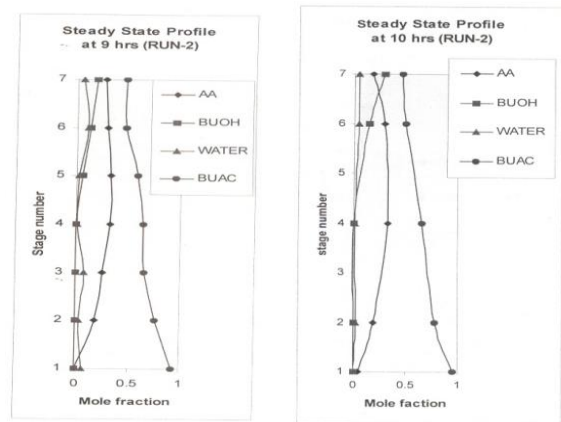

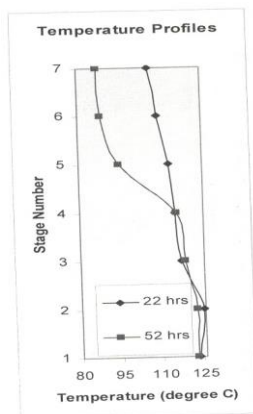**Figure 13:** Concentration profile obtained through reactive distillation column (Run-2) (9, 10 hrs)

Figure 11: Temperature profiles (22 hrs and 52 hrs)
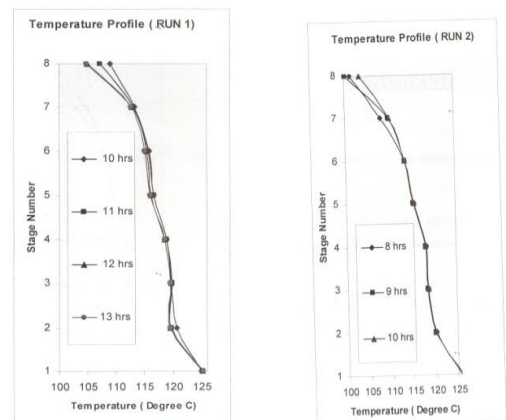

Figure 14: Temperature profiles at steady state (Run-1 and Run-2)

CONCLUSION& SCOPE FOR FUTURE WORK

The esterification of acetic acid with Butanol a reversible process and must be displaced towards the desired ester butyl acetate by a continuous removal of water using the classical concept of reactive distillation (RD). Hence in this work a new approach of RD is studied for the synthesis of BA. Here simultaneous synthesis and separation of the desired product allows limitations due to chemical equilibrium to be overcome. This enhances the rate of reaction. Hence RD is the most promising approach in the case of equilibrium-limited reactions where almost complete conversion of the reactants can be achieved within a single unit due to the integration of chemical conversion and separation. Here the separation gives higher purity product, which reduces the cost of downstream processing.The developed RD has achieved both high purity and high conversion values. This is a significant result compared to the current technology, where similar purity values can be achieved only through a complex series of reactive and separation steps. Amberlyst-15 which is used as an ion exchange resin is found to be good functional material which plays the role of catalyst to boost the reaction rate. High degree of water removal ensures high purity of BA. The esterification of acetic acid with butanol in a batch reactor was studied in details. The kinetics of homogeneous uncatalyzed and heterogeneous catalytic reactions was investigated to understand its contribution in the overall esterification reaction. The effect of reaction paramenters such as temperature, molar concentration, agitation speed and catalyst loading were investigated thoroughly. For interpretation of the kinetics, the observed data were used and the rate parameters were evaluated at each temperature using a batch reactor pseudo homogeneous model. The activation energies for heterogeneous forward and backward reactions were evaluated as 45.59 kJ/mol and 23.39 kJ/mol.

Further the reaction was carried out in RD to study the equilibrium behaviour of reaction. The experiments were carried out for the synthesis of butyl acetate using pilot scale reactive distillation column. The conversion was close to 100%. A considerable time is required to attain the steady state. Ether, the side product can form in reactive distillation column. The formation can be suppressed by adjusting the butanol and acetic acid mole ratios in the feed. The steady state attains in 8-10 hrs. Hence reactive distillation can be effectively used for the synthesis of the butyl acetate. The conversion in reactive distillation is higher than that in conventional steady state reactor. Thus, the use of reactive distillation for this system is justified. The improvement is observed not only through the enhancement in the rate and hence the reduced reactor volume but also through the partial separation of the components involved, thereby reducing the capital and energy cost of downstream processing.

Scope for future work:

Following modifications will be a scope for future work in reactive distillation:

1) Phase separator arrangement: At present, Dean and Stark arrangement used to separate the organic and aqueous phase and it was difficult to maintain the constant levels and a constant eye on the level was required to maintain it. It was affecting the reflux quantity to the column and also the top temperature. This apparatus should be replaced by phase separator arrangement to maintain the constant level and constant reflux.

2) Flow metering pump: A pump was being used to introduce the feed to column. Due to pressure fluctuations in the column, the pump discharge used to change significantly and the manual control of the feed rate is necessary. The pump should be replaced by new electronically driven metering pump that gives constant flow rate irrespective of pressure variation.

3) Increasing condenser capacity: It is observed that during runs there is loss of vapors from the condenser. A new condenser should be introduced in series with the old one which ensures the condensation is complete.

4) Voltage stabilizer: Reactive distillation process is highly sensitive to different parameters. All are affected due to the power supply and results into more time required to attain steady state. A constant power supply is necessary and hence, a dedicated voltage stabilizer should be introduced.

5) Feed locations: At present feed location is at T6. i.e. above the top of reactive section. The effect of feed at different feed locations yet to be studied.

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