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Recovery of dilute acetic acid through esterification in a reactive distillation column

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Abstract

The recovery of acetic acid from its dilute aqueous solutions is a major problem in both petrochemical and fine chemical industries. The conventional methods of recovery are azeotropic distillation, simple distillation and liquid–liquid extraction. Physical separations such as distillation and extraction suffer from several drawbacks. The esterification of an aqueous solution (30%) of acetic acid with *n*-butanol/*iso*-amyl alcohol is a reversible reaction. As excess of water is present in the reaction mixture, the conversion is greatly restricted by the equilibrium limitations. The esters of acetic acid, namely, *n*-butyl acetate and *iso*-amyl acetate, have a wide range of applications. In view of the appreciable value of these esters, the present work was directed towards recovery of 30% acetic acid by reaction with *n*-butanol and *iso*-amyl alcohol in a reactive distillation column (RDC) using macroporous ion-exchange resin, Indion 130, as a catalyst bed, confined in stainless steel wire cages. Experiments were conducted in order to achieve an optimum column configuration for the synthesis of *n*-butyl acetate/*iso*-amyl acetate in an RDC. The effect of various parameters, e.g. total feed flowrate, length of catalytic section, reflux ratio, mole ratio of the reactants, location of feed points and effect of recycle of water were studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Reactive distillation; Esterification; Acetic acid; *n*-Butanol; *iso*-amyl alcohol; *n*-Butyl acetate; *iso*-amyl acetate; Ion-exchange resin

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1. Introduction

Reactive distillation is an emerging technology that has considerable potential as an alternative process for carrying out equilibrium limited liquid phase chemical reactions. It is a unit operation that combines simultaneous chemical reaction and multicomponent distillation in the same vessel, which in turn reduces reactor and recycle costs. Ion-exchange resins (IERs) also find application in reactive distillation columns (RDCs) wherein they play a dual role of catalyst as well as tower packing. Extensive survey of the literature on reactive distillation have been published by Sharma [1], Gaikar and Sharma [2], Buzad and Doherty [3] and Sharma [4].

Reactive distillation processes are now commercially exploited for the manufacture of methyl-*tert*-butyl ether (MTBE), an important anti-knock agent to replace tetraethyl lead in gasoline [5] and methyl acetate which is used as an intermediate in the manufacture of a variety of chemicals, e.g. acetic anhydride [6]. The world's first technology for the commercial production of methylal by the reactive distillation method has been described by Masamoto and Matsuzaki [7]. Recently, acetalization reactions have been studied to synthesise methylal [8], ethylal [9] and 1,3-dioxolane [10] in RDCs. Ion-exchange resin catalysed ketalization of acetone with 1,4- and 1,2-diols was studied by

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Chopade [11] using molecular sieve in RDC. The esterification of formic acid with cyclohexene was also carried out in an RDC with cation exchange resins as catalyst by Saha and Sharma [12].

Both homogeneous and heterogeneous catalysts can be used in RDC. In homogeneously catalysed processes, generally sulphuric acid is used whereas in heterogeneously catalysed reactions, acidic polymeric catalysts such as ion-exchange resins in various forms are used. Acidic polymeric catalysts for their use in RDC must fulfill some essential requirements. A brief review on different forms of catalysts used in RDC was reported by Sharma [4].

Aqueous solutions of acetic acid are produced as by-products of many important processes, such as in the manufacture of cellulose esters, terephthalic acid and dimethyl terephthalate. Moreover, reactions involving acetic anhydride either as a reagent (e.g. acetylations) or as a solvent (e.g. nitrations) can produce a large amount of acetic acid containing waste. Among the industrially relevant examples, the process for the manufacture of cellulose acetate from acetylation of cellulose by acetic acid, acetic anhydride and sulphuric acid, is typically associated with a 35% w/w aqueous solution of acetic acid as a waste stream. Terephthalic acid process involves the concentrations even up to 65% w/w of acetic acid in water [13]. The process for the synthesis of glyoxal from acetaldehyde and nitric acid has a relatively dilute acetic acid stream (typically 13–20% w/w) as a by-product. The wood distillate contains much lower concentrations (1–8% w/w) of acetic acid [14].

The recovery of acetic acid from these streams is a major problem in both the petrochemical and fine chemical industries. The conventional physical separation methods such as distillation and extraction suffer from several drawbacks. Distillation is generally uneconomic because of the high costs involved in vapourising water (the more volatile component) that exists in high proportion but possesses a large latent heat of vapourisation. Extraction is limited by phase separation and distribution of the components involved in the reacting system. In view of these constraints, it is timely to explore alternative methods of recovering the valuable acid. Reactive distillation is a potentially important method of separation for the recovery of acetic acid. Moreover, during the recovery of acetic acid by esterification with *n*-butanol/*iso*-amyl alcohol, a value-added ester is formed. Although, the exact cost estimation depends on several factors, it is likely that reactive distillation may be more economical than conventional processes (distillation and extraction) for the recovery of acetic acid from aqueous streams. An additional column will be required for the complete separation of alcohol and ester. The column would not involve water since it has the highest latent heat and hence the energy cost would be minimised.

Although this process has been successfully commercialised for the manufacture of certain high commodity chemicals, its potential as a separation tool has not been exploited in depth. The esters of acetic acid, namely, *n*-butyl acetate and *iso*-amyl acetate, have a wide range of applications. They are used in large quantities as solvents for plastics, lacquers, resins and gums. *n*-Butyl acetate is primarily used as a solvent for coatings, where its low relative volatility makes it suitable for adjustment of evaporation rate and viscosity. These acetates are also used in the photographic industry, as a reaction medium for adhesives, as solvent for leather dressings, as extraction solvents and as process solvents in various applications and in cosmetic formulations.

In view of the appreciable values of these esters, the present work was directed towards recovery of 30% acetic acid solution by reacting with *n*-butanol and *iso*-amyl alcohol in an RDC using polymeric cationic exchange resins as catalyst. In the present configuration of RDC, the ion-exchange resin catalysed chemical reaction and the multistage distillation occur simultaneously in a continuum, i.e., there is spatial continuity along the length of the column. The effect of variables such as feed flowrate, reflux configuration, length of packed section, molar ratio of reactants, location of the feed point and effect of recycle of water was studied to optimise the reactive distillation column configuration.

2. Previous studies

The esterification of butanol and *iso*-amyl alcohol with acetic acid has been studied by several investigators in the past. Leyes and Othmer [15] were the first to study this reaction in the presence of sulphuric acid as catalyst. They have reported the kinetic data and also presented some useful information on distillation consideration for this system. Gomzi and Paje [16] studied the esterification of *n*-butanol with 98–100% acetic acid in batch mode using Wofatite KPS catalyst with 2–16% of divinyl benzene. Vanko et al. [17] claimed that *n*-butyl acetate containing little acetic acid can be prepared in a column having bubble-cap plates. In sulphuric acid catalysed esterification of 1:0.99 mole ratio of acetic acid to *n*-butanol mixture at reflux temperature of 352.5–353.5 K gave organic phase containing 1.6% H_2O, 8% *n*-butanol, 89–90% *n*-butyl acetate and traces of acetic acid. Combination of reactive distillation with esterification and crude ester refining was studied by Zhang and Liu [18]. Huang and Xu [19] prepared *iso*-amyl acetate by continuous esterification in the presence of strong acidic cation exchange resin catalyst, E-921. Zhicai et al. [20] have recently studied distillation with esterification of butanol and acetic acid experimentally and achieved significant conversion. They have explained the results with mathematical simulation. The example of this reaction has been considered to bring out a novel policy for batch reactive distillation by Venimadhavan et al. [21]. Very recently, Hanika et al. [22] reported a pilot-plant research of butyl acetate synthesis via catalytic distillation. They have performed computer simulation to study the process and to evaluate the experimental data.

It should be noted that most of the literature deals with the esterification reaction in batch mode of operation using 98–100% acetic acid. The dilute acetic acid, in recovery point of view has not been received much attention except the important work reported by Neumann and Sasson [23]. They studied the recovery of acetic acid from 20 to 60% w/w solution through esterification with methanol in a chemorectification column packed with an acidic organic polymer catalyst and obtained about a substantial acetic acid conversion of 70–80%.

3. Materials and catalysts

Acetic acid, *n*-butanol, *iso*-amyl alcohol, sodium hydroxide and phenolphthalein were obtained from s.d. Fine Chem. Coarse sized Indion 130 was obtained from Ion Exchange (India). The physical properties of the cation exchange resin were reported by Saha and Sharma [12].

4. Experimental procedure and apparatus

The experiments were performed in a packed reactive distillation column, shown in Fig. 1. The column consisted of three distinct parts: (i) non-reactive stripping section; (ii) catalytic packed section and (iii) non-reactive enriching section. The diameter of each section of the column was 0.034 m and the length of the different sections of the column was varied for different configurations. The reboiler was heated by a heating mantle and all the sections of the column were provided with a heating blanket, insulation and thermocouple along with an on–off controller to maintain the temperature of the section within ±1 K of the desired set-point. The set-up was also provided with a reboiler, an automatic reflux divider and a water cooled condenser. The reactants were fed through PTFE tubes to the RDC controlling the flow with independent control valves and the flowrates of the feed were monitored volumetrically with the help of capillary manometers. The catalytic section of the column was filled with macroporous ion-exchange resin, Indion 130, catalyst bed, confined in stainless steel wire mesh tea bags. The feeds were introduced at room temperature. Reactants could be continuously fed at any of the feed points F_1–F_7. In a typical experiment, acetic acid was introduced from the top and *n*-butanol/*iso*-amyl alcohol was fed from the bottom to achieve maximum conversion. After starting the reaction, the temperature in each section of the column was noted. The steady state was achieved when all the sections of the columns attained the desired temperatures and the top and bottom products were continuously withdrawn. After the steady state was attained, samples from the top and bottom sections were collected at 5 min interval, weighed and analysed for their composition. Each experiment was continued for 3 h. The flowrates of the feed, bottom and overhead were measured and a complete material balance was performed.

5. Analysis

Acetic acid, *n*-butanol, water and *n*-butyl acetate were analysed using gas chromatograph (Chemito 8510, Toshniwal brothers, India), fitted with a ther-

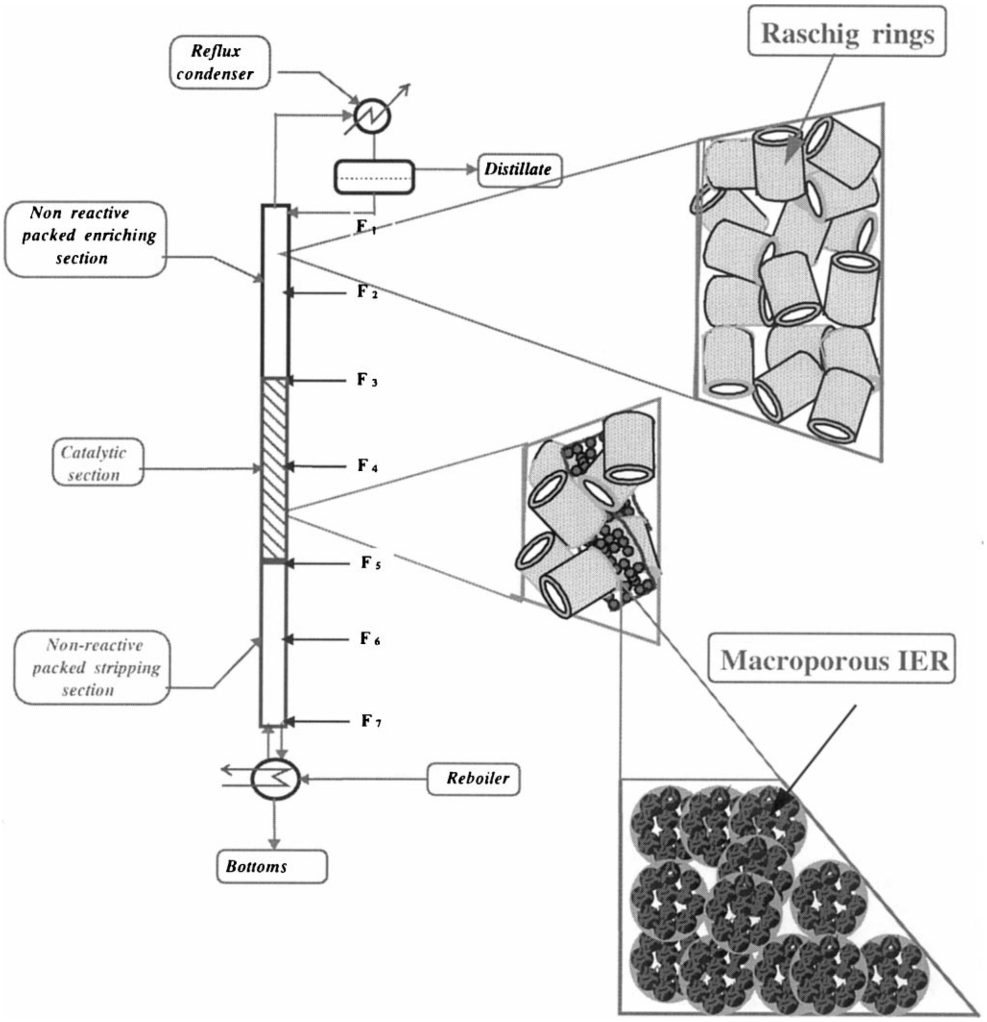


Fig. 1. Schematic diagram of a reactive distillation column.

mal conductivity detector (TCD). Two identical 2.0 m×0.003 m stainless steel columns packed with Porapak Q were used with hydrogen as carrier gas at a flowrate of 5×10^{-7} m^3/s. Injector and detector block temperatures were maintained at 473 K. The oven temperature was maintained isothermal at 443 K. Acetic acid concentration was cross-checked by titrating the sample with dilute 0.1 (N) sodium hydroxide solution using phenolphthalein as indicator.

In the reaction of *iso*-amyl alcohol with acetic acid, two phases were obtained at the bottom and distillate was collected at the top. The analysis of *iso*-amyl-acetate–*iso*-amyl-alcohol–water was carried out by gas chromatography fitted with a thermal conductivity detector (TCD). Two identical 4.0 m×0.003 m stainless steel columns packed with OV 210 on Chromosorb WHP were used with hydrogen as carrier gas at a flow rate of 5×10^{-7} m^3/s. Injector and detector block temperatures were maintained at 483 K. The oven temperature was maintained isothermal at 373 K. Acetic acid concentration was cross-checked by titrating the sample with dilute 0.1 (N) sodium hydroxide solution using phenolphthalein as indicator.

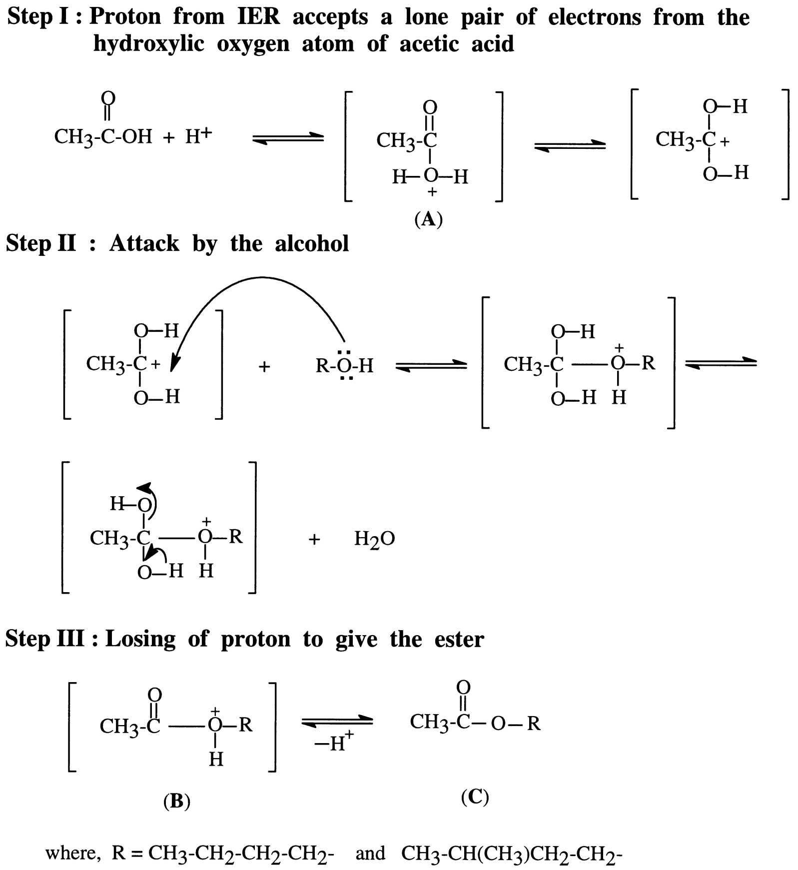


Fig. 2. Mechanism of reaction.

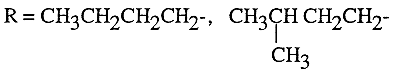
6. Mechanism of reaction

Acetic acid reacts with *n*-butanol and *iso*-amyl alcohol in the presence of cation exchange resin catalyst to give the corresponding ester. These esterification reactions are equilibrium limited chemical reactions.

The overall reaction is

$$CH_3COOH + ROH \rightleftharpoons CH_3COOR + H_2O$$

where



$$R = CH_3CH_2CH_2CH_2\text{-},\quad CH_3\underset{\substack{|\\CH_3}}{C}H\,CH_2CH_2\text{-} \qquad (1)$$

In step I, a proton from cation exchange resin accepts a pair of unshared electrons from the hydroxylic oxygen atom of acetic acid to form an oxonium ion (A). In step II, this is attacked from the rear by the alcohol with expulsion of water to form the substituted oxonium ion (B), which loses a proton to give the ester (C) in step III. The proton required in the first step is regenerated in the last step. All the steps are reversible and an equilibrium is established. The mechanism of the reaction is shown in Fig. 2.

7. Results and discussion

The esterification of 30% aqueous solution of acetic acid with *n*-butanol and *iso*-amyl alcohol is a reversible reaction. As excess of water was present in the reaction mixture, the conversion was greatly

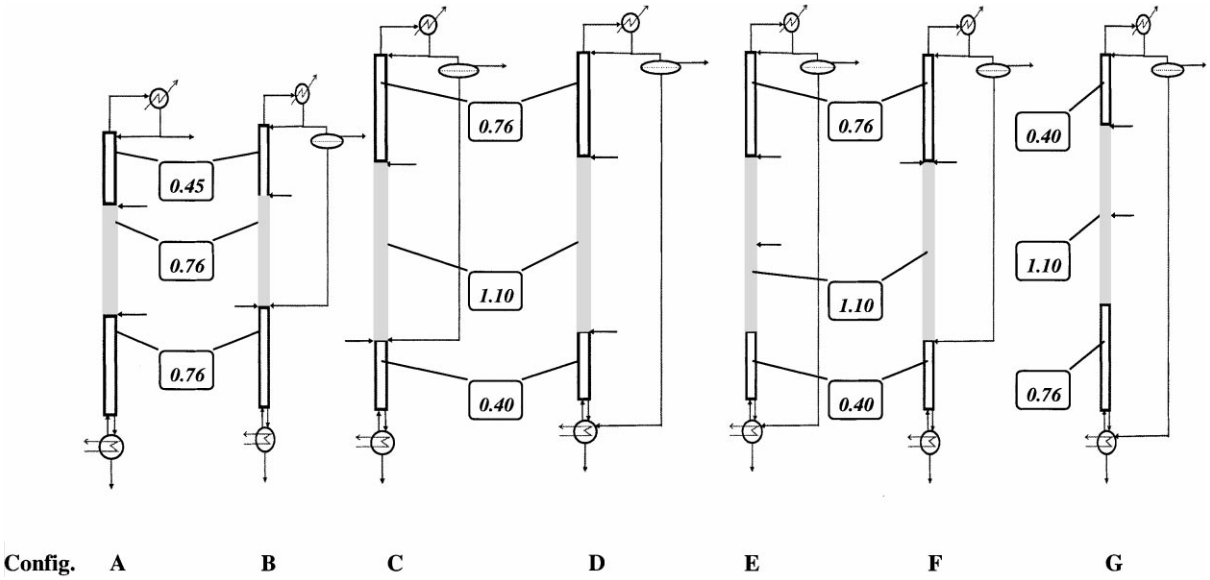


Fig. 3. Various configurations adopted for the recovery of aqueous acetic acid with *n*-butanol.

restricted by the equilibrium limitation. In the recovery of 30% acetic acid with *n*-butanol, lower boiling azeotropes, such as *n*-butyl-acetate–*n*-butanol–water, *n*-butanol–water, *n*-butyl-acetate–water formed at a temperature range 362–363 K. At the top of RDC, a ternary mixture of *n*-butyl-acetate–*n*-butanol–water, boiling at a constant temperature of 362 K was obtained. In the reaction with *iso*-amyl alcohol, *iso*-amyl-acetate–*iso*-amyl-alcohol–water, *iso*-amyl-alcohol–water and *iso*-amyl-acetate–water formed lower boiling azeotropes, at 368.5 K. A ternary mixture of *iso*-amyl-acetate–*iso*-amyl-alcohol–water boiling at constant temperature of 368.5 K was obtained as an overhead product.

Experiments were conducted in order to achieve an optimum column configuration for the synthesis of *n*-butyl acetate/*iso*-amyl acetate in an RDC. Various parameters, e.g. total feed flowrate, length of catalytic section, reflux ratio, mole ratio of the reactants, location of feed points were studied. On the acetic acid recovery point of view, the optimal configuration should give the highest conversion of acetic acid with minimum concentration of acetic acid at the top and minimum concentration of *n*-butanol and ester at the bottom. An additional column will be required for the complete separation of alcohol and ester.

7.1. Typical configuration (TC)

All the experiments were carried out in the following typical configuration unless otherwise stated. The various configurations adopted for this study have been shown in Figs. 3 and 4 and mentioned in Table 1.

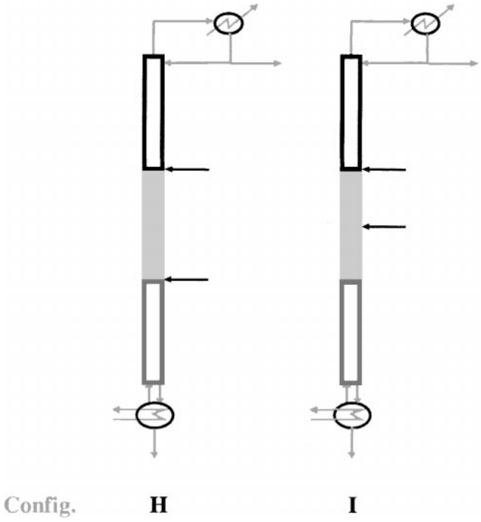


Fig. 4. Various configurations adopted for the recovery of aqueous acetic acid with *iso*-amyl alcohol.

Table 1

Various configurations adopted for synthesis of *n*-butyl acetate/*iso*-amyl acetate in an RDC[a]

	A	B	C	D	E	F	G	H	I
Section I, length (m)	0.45	0.45	0.76	0.76	0.76	0.76	0.40	0.76	0.76
Section II, length (m)	0.76	0.76	1.10	1.10	1.10	1.10	1.10	0.76	0.76
Section III, length (m)	0.76	0.76	0.40	0.40	0.40	0.40	0.76	0.76	0.76
Acetic acid, feed position	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)	Top of section II (F_3)
n-Butanol/*iso*-amyl alcohol, feed position	Bottom of section II (F_5)	Bottom of section II (F_5)	Bottom of section II (F_5)	Bottom of section II (F_5)	Midway of section II (F_4)	Top of section II (F_3)	Midway of section II (F_4)	Bottom of section II (F_5)	Midway of section II (F_4)
Reflux	Both phases	Aqueous phase at the bottom of section II (F_5)	Aqueous phase at the bottom of section II (F_5)	Aqueous phase in reboiler, F_7	Aqueous phase in reboiler, F_7	Aqueous phase at the bottom of section II (F_5)	Aqueous phase in reboiler, F_7	Single phase	Single phase

[a] Configurations A to G: recovery of 30% aqueous acetic acid with *n*-butanol; configurations H and I: recovery of 30% aqueous acetic acid with *iso*-amyl alcohol.

Typical configuration (shown in Fig. 1)
Section I: Non-catalytic enriching section
Section II: Catalytic reactive section
Section III: Non-catalytic stripping section
30% Aqueous acetic acid feed: liquid at room temperature, concentration 30% w/w
n-Butanol feed: liquid at room temperature
Condenser: total condenser, condensate liquid at bubble point
Reflux: saturated liquid at bubble point
Reflux ratio: 2
Mode of operation: counter-current

7.2. Effect of total feed flowrate

The total feed rate was varied from 150 to 300 ml/h keeping the mole ratio of the reactants constant. It was found that at higher feed flowrate, the conversion of acetic acid decreased since at high flowrate, the residence time of the reactant in the column was lowered and thus all further experiments were carried out at an optimum total feed flowrate of 192 ml/h. The optimal total flowrate was the same for *n*-butanol and *iso*-amyl alcohol. No by-product existed above the detectable limits over the range of residence time employed in this work. However, the conversion of acetic acid decreased with an increase in flowrate from 192 to 300 ml/h. This is a typical observation for the reactions that are kinetically controlled.

The work by Song et al. [24] on the synthesis of methyl acetate in the presence of ion-exchange resin clearly shows that the reaction is kinetically controlled (i.e., slow). Esterification of acetic acid with *n*-butanol/*iso*-amyl alcohol is slower than that with methanol and on this ground the reaction of interest is slow enough to be categorised as kinetically controlled reaction. The reaction is slower compared to distillation (mass transfer) and the rate of recovery is governed by the kinetic features such as residence time, hold up, intrinsic rate constant, etc.

7.3. Effect of reflux configuration

In the recovery of 30% aqueous acetic acid with *n*-butanol, it was expected that *n*-butanol would move upwards in the column as a binary azeotrope with water (boiling at 362 K). Few runs were carried out in configuration A where it was thought that the length between F_5 and F_6 of the stripping section would be used to form this azeotrope and the length between F_6 and F_7 would be used for stripping of *n*-butanol. Acetic acid being the highest boiling component of the system fed at the top of the catalytic section. The introduction of water at the bottom of the reactive section lifts butanol up and minimises its concentration in the bottom stream. The availability of more butanol in the reactive section thus facilitates more conversion.

At the top of the RDC, a ternary mixture of *n*-butyl-acetate–*n*-butanol–water, boiling at 362 K was obtained. The distillate was separated in two phases of which the aqueous phase was refluxed back at the top of the distillation unit (F_1). The distillate contained very small amount of acetic acid (up to 0.13%) and the bottom contained an insignificant amount of butyl acetate (up to 0.08%). The maximum acetic acid conversion of 45% was achieved in this configuration.

The configuration B adopted in this study was same as configuration A, only the distillate was separated in two phases of which the aqueous phase was fed back at the bottom of section II (F_5). Due to this change in configuration, up to 52.8% conversion of acetic acid was achieved. No *n*-butanol was obtained at the bottom fraction. A homogeneous mixture was obtained at the bottom in all the experiments. The enhancement of the conversion of acetic acid passing from configuration A to B can perhaps be attributed to a lower average water content of water in the reactive section of the column. The results are given in Table 2.

7.4. Effect of length of packed section

In order to increase the residence time of the reactants in the column, the catalytic packed section was increased to 1.10 mm from 0.76 m and the length of the non-catalytic enriching section was also increased to 0.76 m from 0.45 m (configuration C). However, no significant change in the conversion of acetic acid was realised with the change in configuration from B to C. The results are given in Table 2. A twofold objective is met by adopting this configuration.

7.5. Effect of mole ratio

The mole ratio of the reactants plays an important role in determining the conversion, distillate purity and

Table 2
Composition of various components (wt.%) studied at different configurations

Configuration	Mole ratio (AcOH:alcohol)	% Conv. of AcOH	Top comp.				Bottom comp.			
			AcOH	Alcohol	Water	Ester	AcOH	Alcohol	Water	Ester
A	1:2	45.0	0.13	58.16	18.64	23.07	27.56	2.06	70.38	0.08
B	1:2	52.8	0.00	59.6	14.1	26.3	23.3	0.00	76.6	0.00
C	1:2	52.7	0.00	62.2	15.1	22.7	23.3	0.00	76.7	0.00
D	1:2	57.6	0.00	39.6	18.0	42.4	13.0	21.9	65.1	0.00
E	1:2	35.4	0.00	62.0	15.4	22.6	18.9	2.0	79.1	0.00
F	1:2	32.4	0.00	62.9	14.96	22.14	24.62	11.47	63.91	0.00
G	1:2	54.0	0.00	55.2	12.6	32.2	16.0	12.1	71.9	0.00
H	1:2	31.88	0.60	75.76	1.65	21.99	Aqueous 13.80	5.40	80.80	0.00
							Organic 1	76.48	8.87	0.86
I	1:2	50.90	0.33	72.70	0.21	26.77	Aqueous 20.08	1.94	77.98	0.00
							Organic 19.85	72.19	7.93	0.03

the relative weight fractions of the top and bottom. The mole ratio of acetic acid to *n*-butanol was studied at 1:1.5, 1:2 and 1:3. All the reactions were carried out in configuration C.

It can be seen from Table 3, that maximum conversion of 52.7% of acetic acid was achieved at 1:2 mole ratio of acetic acid to *n*-butanol. It is evident that 1:2 mole ratio is optimum and all further experiments were carried out at this mole ratio. With an increase in mole ratio of acetic acid to *n*-butanol, from 1:3 to 1:2, the conversion of acetic acid increased from 36 to 52.7%. For 1:1.5 and 1:2 mole ratios of the reactants, no *n*-butanol was obtained at the bottom. However, at 1:3 mole ratio of acetic acid to *n*-butanol, 8% *n*-butanol was obtained at the bottom. In all the cases, no trace of acetic acid was obtained at the top of RDC unit. It was also observed that the percent fraction (w/w) of water in the distillate was varied from 15.1 to 16.6% with the change in mole ratio from 1:2 to 1:3. Since *n*-butanol forms binary azeotrope with water and ternary azeotrope with water–*n*-butyl acetate at 362.5 and 365.5 K, respectively, it is expected that at lower mole ratio, i.e., at 1:1.5, almost all the *n*-butanol forms azeotrope and moves upwards. Hence, the availability of *n*-butanol to react with acetic acid decreased.

Table 3
Effect of mole ratio of acetic acid to *n*-butanol

Configuration	Mole ratio (acetic acid:*n*-butanol)	Conversion (%) of acetic acid
C	1:1.5	40.1
C	1:2	52.7
C	1:3	36.2

7.6. *Effect of feed position*

7.6.1. *Counter-current versus co-current*

The feed positions of acetic acid and *n*-butanol is also a very important parameter in the operation of the reactive distillation column. For the system to operate optimally, provision should be made for maximum contact area between the reactants so that more of the column is used as a reactor and not as a distillation unit only.

The configuration C was adopted for this experiment in counter-current mode with recycle of water. The distillate was separated in two phases of which the aqueous phase was refluxed back at the bottom of the catalytic packed section. The same experiment was carried out in co-current mode of operation (configuration F), where both the feeds were introduced at the top of section II (F_3). The results are given in Table 2. It was found that with the change in the mode of operation from co-current to counter-current, with 1:2 mole ratio of acetic acid to *n*-butanol, the conversion of acetic acid increased from 32.4 to 52.7%. Also the residual concentration of *n*-butanol in the bottom was quite high as compared to that achieved in the case of counter-current mode. Hence, counter-current mode of operation was preferred to the co-current mode. In this reactive system the reactants acetic acid and butanol behave quite differently. Since butanol forms minimum boiling azeotropes with water and butyl acetate, and since there is plenty of water present in the column it has a volatile character compared to acetic acid. It is reported and proved that such reactants should preferably fed at different locations to the reactive distillation column to obtain better efficiency [25].

7.6.2. Change in feed point for the synthesis of iso-amyl acetate

It is to be noted that the experiments with *iso*-amyl alcohol were carried out to compare the performance with *n*-butanol for the recovery of 30% acetic acid solution in an RDC. In the recovery of 30% acetic acid with *n*-butanol, lower boiling azeotropes, such as *n*-butyl-acetate–*n*-butanol–water, *n*-butanol–water, *n*-butyl-acetate–water formed at a temperature range 362–363 K. At the top of RDC, a ternary mixture of *n*-butyl-acetate–*n*-butanol–water, boiling at a constant temperature of 362 K was obtained. Here, *iso*-amyl-acetate–*iso*-amyl-alcohol–water; *iso*-amyl-alcohol–water; *iso*-amyl-acetate–water form lower boiling azeotropes at 368.2 K. Acetic acid, which does not form any azeotrope in this system, becomes the highest boiling component, hence was fed at the top of the catalytic section (configuration H).

At the top of RDC, a ternary mixture of *iso*-amyl-alcohol–*iso*-amyl-acetate–water was obtained. The distillate contained small amount of acetic acid (<1%). At the bottom of RDC, two phases were obtained and a maximum conversion of 32% of acetic acid was achieved at the end of the reaction. In the organic phase of the bottom product, small amount (<1%) of ester and ∼76% *iso*-amyl alcohol were detected. However, the aqueous phase contained ∼5% *iso*-amyl alcohol.

Since by adopting the configuration H, ∼32% conversion of acetic acid was achieved, the feed point of *iso*-amyl alcohol was changed. In configuration I, the feed point of *iso*-amyl alcohol was changed from F_5 (bottom of catalytic section) to F_4 (midway of the catalytic section). In this case 51% conversion of acetic acid was realised at the end of reaction. Unlike configuration H, in this configuration ∼20% *iso*-amyl alcohol was detected in the aqueous and organic phases of the bottom product. The concentration of *iso*-amyl alcohol dropped down to ∼2% in the aqueous phase of the bottom product. The results are shown in Table 2.

7.7. Effect of recycle of water

The effect of with and without recycle of water was studied to increase the conversion of acetic acid for its recovery from aqueous solution. For reaction with recycle of water, the distillate was separated in two phases of which the aqueous phase was fed back to the bottom of section II (F_5) and the reaction was conducted in configuration B. The same reaction was conducted in configuration D where the distillate was separated in two phases of which the aqueous phase was blended with the bottoms.

Table 2 shows that without recycle of water, the conversion of acetic acid increased to 57.6% as compared to 52.8% with recycle of water. This can be due to the minor quantity of *n*-butanol that was stripped as an azeotrope with water. However, without recycle of water, 21.9% w/w of *n*-butanol was obtained at the bottom, whereas with recycle of water, no *n*-butanol was obtained at the bottom of the RDC unit.

In order to reduce the concentration of *n*-butanol at the bottom, another set of experiments were conducted following configuration E where the feed position of *n*-butanol was changed from bottom of section II (F_5) to an intermediate point in section II (F_4), which was 0.4 m above the bottom of section II (F_5). Although the concentration of *n*-butanol was brought down to 2%, the conversion of acetic acid was reduced to 35.4%. This decrease in conversion of acetic acid may be because of introduction of *n*-butanol feed at an intermediate point in the catalytic section as compared to the previously adopted counter-current mode of operation (configuration D).

Hence it was thought that an increase in the length of non-catalytic stripping section would give desired separation without affecting conversion level. Since it was found that the length of enriching section was more than sufficient, its length was reduced to 0.4 m and the length of stripping section increased to 0.76 m. The length of catalytic packed section was kept the same (configuration G). Acetic acid was fed at the top of section II (F_3) and *n*-butanol was fed at the midway of catalytic section II, i.e., at F_4. Configuration G was adopted with a notion that it would improve the acetic acid conversion as well as reduce the *n*-butanol content at the bottom of the column. However, in this configuration 54% conversion of acetic acid was achieved and the concentration of *n*-butanol at the bottom was

12.1%. The top and bottom compositions are listed in Table 2. On the acetic acid recovery point of view, the optimal configuration should give the highest conversion of acetic acid with minimum concentration of acetic acid at the top and minimum concentration of *n*-butanol and ester at the bottom. Considering all the above factors it can be concluded that the optimal configuration is B.

8. Conclusions

The recovery of 30% aqueous solution of acetic acid by esterification with *n*-butanol and *iso*-amyl alcohol was performed in a reactive distillation column using macroporous Indion 130 cation exchange resin as a catalyst bed, confined in stainless steel wire mesh tea bags. The reactions were found to be equilibrium limited. The recovery of acetic acid was enhanced by carrying out the reaction in a reactive distillation column. The effect of various parameters, e.g. feed rate, location of feed points, reflux ratio, mole ratio of the reactants, etc. were studied and analysed. In a typical configuration, at 1:2 mole ratio of acetic acid to *n*-butanol, ∼58% conversion of acetic acid was achieved. In a typical run, with 1:2 mole ratio of acetic acid to *iso*-amyl alcohol, ∼51% conversion of acetic acid was achieved. The best result was obtained when the column was operated in counter-current mode. The modelling work to explain the results obtained in this work will require the rigorous data on intrinsic kinetics and phase equilibria. It should be noted that reacting system is composed of four phases (solid (catalyst)–liquid–liquid–vapour) and such systems are rarely dealt with for the theoretical analysis of reactive distillation.

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References

[1] M.M. Sharma, J. Separat. Process. Technol. 6 (1985) 9.
[2] V.G. Gaikar, M.M. Sharma, Separat. Purif. Meth. 18 (1989) 111.
[3] G. Buzad, M.F. Doherty, Trans. Inst. Chem. Engrs. 70 (1992) 448.
[4] M.M. Sharma, React. Polym. 26 (1995) 3.
[5] L.A. Smith, US Patent No. 4,978,807 (1990).
[6] C.G. Mayfield, V.H. Agreda, Energy Prog. 6 (1986) 214.
[7] J. Masamoto, K. Matsuzaki, J. Chem. Eng. Jpn. 27 (1994) 1.
[8] A.K. Kolah, S.M. Mahajani, M.M. Sharma, Ind. Eng. Chem. Res. 35 (1996) 3707.
[9] S.P. Chopade, M.M. Sharma, React. Funct. Polym. 32 (1997) 53.
[10] S.P. Chopade, M.M. Sharma, React. Funct. Polym. 34 (1997) 37.
[11] S.P. Chopade, M.M. Sharma, React. Funct. Polym. (1999), 42 (1999) 201.
[12] B. Saha, M.M. Sharma, React. Funct. Polym. 28 (1996) 261.
[13] V. Van Brunt, US Patent No. 5,175,357 (1992).
[14] F.S. Wagner, in: I. Kroschwitz (Ed.), Kirk–Othmer Encyclopedia of Chemical Technology, Vol. 1, 4th Edition, 1991, 132 pp.
[15] C.E. Leyes, D.F. Othmer, AIChE J. 41 (1945) 157.
[16] Z. Gomzi, E. Paje, Kem. Ind. 19 (1970) 249, Chem. Abstr. 74:12568.
[17] M. Vanko, L. Komora, J. Antalik, Czech. Patent No. 254,048 (1986), Chem. Abstr. 111:59983.
[18] J. Zhang, Y. Liu, Shiyou Huagong 20 (1991) 527, Chem. Abstr. 116:154167.
[19] L. Huang, H. Xu, Xiangtan Daxue Ziran Kexue Xuebao 15 (1993) 119, Chem. Abstr. 121:258364.
[20] Y. Zhicai, C. Xianbao, G. Jing, Chem. Eng. Sci. 53 (1998) 2081.
[21] G. Venimadhavan, M.F. Malone, M.F. Doherty, Ind. Eng. Chem. Res. 38 (1999) 714.
[22] J. Hanika, J. Kolena, Q. Smejkal, Chem. Eng. Sci. 54 (1999) 5205.
[23] R. Neumann, Y. Sasson, Ind. Eng. Chem. Process Des. Dev. 23 (1984) 654.
[24] W. Song, G. Venimadhavan, J.M. Manning, M.F. Malone, M.F. Doherty, Ind. Eng. Chem. Res. 37 (1998) 1917.
[25] D. Barbosa, M.F. Doherty, Chem. Eng. Sci. 43 (9) (1988) 2377.