Esterification of Acetic Acid with Butanol: Operation in a Packed Bed Reactive Distillation Column

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The esterification reaction between acetic acid and butanol was investigated in a reactive distillation column. The thermodynamic aspects of considered system are discussed, equilibrium constant, vapor pressures and UNIQUAC interaction parameters were investigated. Reactive distillation experiments were carried out to provide high purity butyl acetate. For this purpose, a 2 m column with nonreactive and reactive zones filled with Amberlyst 15 and Raschig rings, were used in the experiments. Several operating conditions such as total feed flow rate, molar ratio of butanol to acetic acid, amount of catalyst and reboiler temperature and three different column configurations were realized experimentally. The experimental optimum values of these parameters obtained were 1.6 mol h^{-1}, 1, 25 g and 383 K, respectively within the range of study. The butyl acetate purity of 82 % and acetic acid conversion of 80.5 % were obtained at the optimum operating conditions.

Key words:
Acetic acid, esterification**,** butyl acetate, reactive distillation, Amberlyst 15

Introduction

Reactive distillation is a combination of reaction and distillation in a single vessel owing to which it enjoys a number of specific advantages over the 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 of difficult separations and the avoidance of azeotropes are a few of the advantages that reactive distillation offers.[1]

Reactive distillation has received increasing attention over the past several years as a promising alternative to conventional processes. Especially for equilibrium-limited and consecutive reactions, reactive distillation offers distinct advantages through the direct removal of the reaction products by distillation. Therefore, conversions far beyond equilibrium conversions and higher selectivities can be obtained, leading to significantly lower investment and operating costs.[2]

The shortcomings of reactive distillation include greater complexity in design and process control, often involving multiple steady states, and high nonlinearity due to the strong interaction between process variables. Moreover, the operating window of reactive distillation processes must be compatible with the thermal stability of the catalyst in order to ensure long catalyst life. Reactive distillation also requires a significant research and development effort in order to develop and successfully scale up a promising process.[3]

Organic solvents such as acetate esters are important chemicals for many industries. *n*-Butyl acetate having low toxicity and low environmental impact is used in large quantities in paint; lacquer industry and coating manufacture.[2] It is usually synthesized with esterification reaction in the presence of a strongly acidic catalyst such as ion exchange resin,[4] sulphated zirconia[5] or alumina supported tungstophosphoric acid[6] in a liquid phase system. Since the reaction is equilibrium-limited, the use of reactive distillation, which combines the reaction and separation functions in one column, is an attractive option.[7]

Synthesis of butyl acetate is commonly carried out by esterification of butanol with acetic acid in the presence of a suitable acid catalyst. In our previous study,[4] we investigated the esterification reaction between acetic acid and butanol catalyzed by Amberlyst 15 in a batch reactor and the kinetic expression of this reaction was obtained as follows:

$$-r_A = \frac{m_{cat}\, 2.46 \cdot 10^5 \exp\left(-\dfrac{36963}{RT}\right) K_{alcohol}\left(a_{acid}\, a_{alcohol} - \dfrac{1}{K}\, a_{ester}\, a_{water}\right)}{(1 + K_{alcohol}\, a_{alcohol} + K_{water}\, a_{water})}$$

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Temperature dependency of adsorption constants were found to be:

$$K_{alcohol} = 0.00107 \exp\left(-\frac{2594}{T}\right)$$

$$K_{water} = 0.05346 \exp\left(-\frac{1365}{T}\right)$$

Reactive distillation has been successfully used and investigated in the past for several reactions such as etherification, esterification, hydrogenation, hydrodesulphurization and polymerization. Especially, some investigations of different process alternatives for the production of butyl acetate have been performed. Löning et al.[8] focused their attention on *n*-butyl acetate hydrolysis and analyzed reactive residue curve maps to gain insights into the different kinds of singular points present in the system. Hanika et al.[9] investigated the esterification of butanol with acetic acid by reactive distillation. These authors included only a few data about pilot-plant experiments. Steinigeweg and Gmehling[2] also investigated the thermodynamic aspects, reaction kinetics and pilot-plant experiments of butyl acetate synthesis.

Since the esterification reaction is equilibrium limited, the use of the reactive distillation is an attractive method by removing products from the reaction mixture, which leads to an increase in the reactant conversion.[10] In addition, it was reported that a ternary azeotropic mixture of acetate, alcohol and water is found,[11] thus resulting in difficulties in downstream separation if a traditional production process is utilized.

Recently, a number of researches have been focused on the implementation of reactive distillation as a promising alternative to produce value-added chemicals, esters. In comparison with the traditional method of separation that follows the reaction process, performing the chemical reaction and separation in a single reactive distillation column offers advantages to produce a valuable product with reduced capital and energy costs. Following this approach, applications of reactive distillation operations in the chemical industry has received much attention.[12–14]

Both homogeneous and heterogeneous catalysts can be used in reactive distillation operations. In homogeneously catalyzed processes, generally sulfuric acid is used, whereas in heterogeneously catalyzed reactions, acidic polymeric catalysts such as ion-exchange resins in various forms are used. Acidic polymeric catalysts must fulfill some essential requirements for their use in reactive distillation column. A brief review on different forms of catalysts used in reactive distillation column was reported by Sharma et al.[15]

Although significant research exists on the subject, there are still areas to be clarified from the points of both different column configurations and operating conditions affecting the reaction and separation processes. The aim of this work is the study of the production of butyl acetate by esterification of acetic acid with butanol in a reactive distillation column. For this purpose, the esterification of butanol with acetic acid is studied for three different column configurations and also the effects of some variables such as total feed flow rate, reboiler temperature, molar ratio of butanol to acetic acid and amount of catalyst were investigated for a wide range.

Thermodynamical aspects for butanol-acetic acid esterification system

Equilibrium constant

Equilibrium constant can be calculated using thermodynamic data. Firstly, equilibrium constant at a reference temperature is found from standard Gibbs energy of reaction and equilibrium constants at different temperatures are determined using the integrated form of Van't Hoff equation:

$$\ln K(T_0) = -\frac{\Delta G_0}{RT_0}$$

$$\ln K(T) = \ln K(T_0) - \frac{\Delta H_0}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

For the esterification of butanol with acetic acid, using the thermodynamic data, the equilibrium constants were calculated. Constant enthalpy of reaction is assumed because of the small temperature interval investigated.

In our previous study,[5] experimental equilibrium constants were found at temperatures of 328, 333, 338 and 343 K. Experimental and theoretical equilibrium constant values as a function of inverse of temperature are shown in Fig. 1. The decrease in *K* values with increase in temperature shows that this esterification is exothermic. Enthalpy of reaction was calculated for this reaction and found as –18.7 kJ mol^{–1}.

Activities of components

In the calculations of equilibrium constants the UNIQUAC model was used to determine the activity coefficients in the liquid phase because of the strong nonideality of the reaction mixture. The vol-
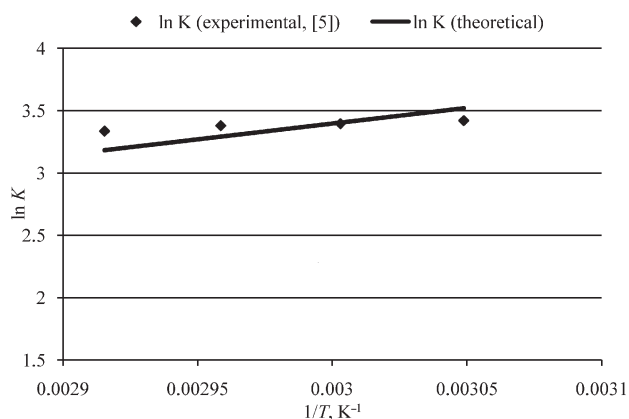
F i g . 1 – *Plot of chemical equilibrium constant*

T a b l e 2 – *Stationary points in the system*

Pure components or azeotropes	Mole fractions				Boiling point/K
	AcAc	BuOH	BuAc	H$_2$O	
AcAc	1				391.05
BuOH		1			390.85
BuAc			1		399.25
H$_2$O				1	373.15
AcAc-H$_2$O	0.5260	0.4740			395.40
BuOH-BuAc		0.7329	0.2671		389.41
BuOH-H$_2$O		0.2218		0.7782	366.99
BuAc-H$_2$O			0.2876	0.7134	364.05
BuOH-BuAc-H$_2$O	0.0551	0.24		0.7049	363.88

ume, area parameters and UNIQUAC equations were given in our previous study.[5]

Volatilities of components

To model the temperature dependence of vapor pressures, the modified Antoine equation was used.

Volatilities of components and relative volatilities by choosing butyl acetate as reference component are calculated and tabulated in Table 1. As shown in Table 1, the relative volatilities of the components are in the following order:

water > acetic acid > butanol > butyl acetate.

The products water and butyl acetate are the lightest and heaviest components, respectively, with the reactants acetic acid and butanol as middle boilers. The thermodynamic behavior indicates that we should remove water from the distillate and obtain heavy butyl acetate from the bottoms. For this system, reactive distillation is a good candidate because the volatility of reactants is sandwiched between the volatility of the products.

T a b l e 1 – *Volatilities of components of acetic acid – butanol esterification system*

Component	Butanol	Acetic acid	Butyl acetate	Water
Volatility (*)	0.5103	0.5553	0.4398	0.9940
Relative volatility	1.160	1.263	1	2.260

(*) based on bar and *K* as pressure and temperature units.

Singular points

Normal boiling point of pure components and azeotropes in the system is shown in Table 2. Butyl acetate creates a low-boiling ternary heterogeneous azeotropic mixture with butanol and water, which is separated at the top of the column. Upon condensa-

tion, it separates into two liquid phases in the decanter. The organic phase consists of butyl acetate, butanol, and water, which is refluxed back to the column, whereas the aqueous phase (mainly water) is removed as a distillate.

Experimental study

Materials and catalyst

Butanol (Merck) and acetic acid (Merck) were used as reactants experiments. The cation exchange resin in the H$^+$ form, Amberlyst 15, was obtained from Rohm and Haas Co. The properties of Amberlyst 15 were tabulated in Table 3.

T a b l e 3 – *Properties of Amberlyst 15*

Manufacturer	Rohm & Haas
Polymer type	Macroreticular
Matrix type	Styrene divinyl benzene (DVB)
Functional group	Sulphonic acid
Ionic form	H$^+$
Total exchange capacity (meq/mL)	1.8
Crosslinking/% DVB	20
Moisture content/% mass	1.6
Maximum operating temperature/°C	120

Experimental setup

The experiments were performed in a glass column operating at atmospheric pressure. The column with a diameter of 4 cm and packing height of 2 m was constructed. The reaction section of column

had a height of 1m; it was filled with a combination of Raschig glass rings having an average diameter and length of 6 mm, and catalyst, Amberlyst 15. The enriching and stripping sections of the column were filled only with Raschig glass rings. A reboiler completed with PID temperature indicating controller was used to supply vapors in the column. The column, reboiler and condenser were insulated using fiberglass (glass wool) to prevent heat losses. Two peristaltic pumps (Masterflex, multichannel pump-07519) were used to adjust the flow rates of butanol and acetic acid. Temperatures through the column and in reboiler were measured during the experiments and liquid samples were taken from the different points of column by using a syringe.

Experimental procedure

The mixture of acetic acid and butanol was fed into the reboiler of the column and reboiler duty was ramped to the desired temperature at atmospheric pressure. The column was operated at total reflux for 30 minutes, then the acetic acid and butanol were fed into the column. During the experiments, flow rates of top and bottom products were measured periodically. Steady state condition was reached when the flow rates of top and bottom products became constant. The vapor leaving the top of the column condensed, and the water phase was withdrawn while the organic phase was recycled into the column. Pure butyl acetate was withdrawn from the column reboiler. Samples from reboiler and different points through the column were taken and analyzed using a gas chromatograph.

Analysis

A Hewlett-Packard 6890 gas chromatograph was used to determine the composition of the samples. The gas chromatograph column was HP-FFAP polyethylene glycol TPA equipped with a series of connected thermal conductivity and flame ionization detectors to detect the compounds in the same run. Helium was used as carrier at a flow rate of $6.8 \cdot 10^{-8}$ m^3 s^{-1}. Injector, detectors and oven temperature were 473.15, 503.15 and 423.15 K, respectively.

Results and discussion

Effect of column configuration

In general, reactive distillation operations are performed by countercurrent flow of reactants. Reactant having a low boiling point is fed to the bottom of the column and the other reactant is fed to the top of the column. Thus, reactant having a low

boiling point vaporizes then reacts with the other reactant. However, since the boiling point of acetic acid is very close to that of butanol, in the study the optimal feed location must be determined by making different experimental studies.

Operating conditions of the different runs were divided into three setups depending on the mode in which the feed was introduced into the column as a mixture of reactants or the reactants were fed separately. In Fig. 2, the schematic representations of three column configurations are shown.
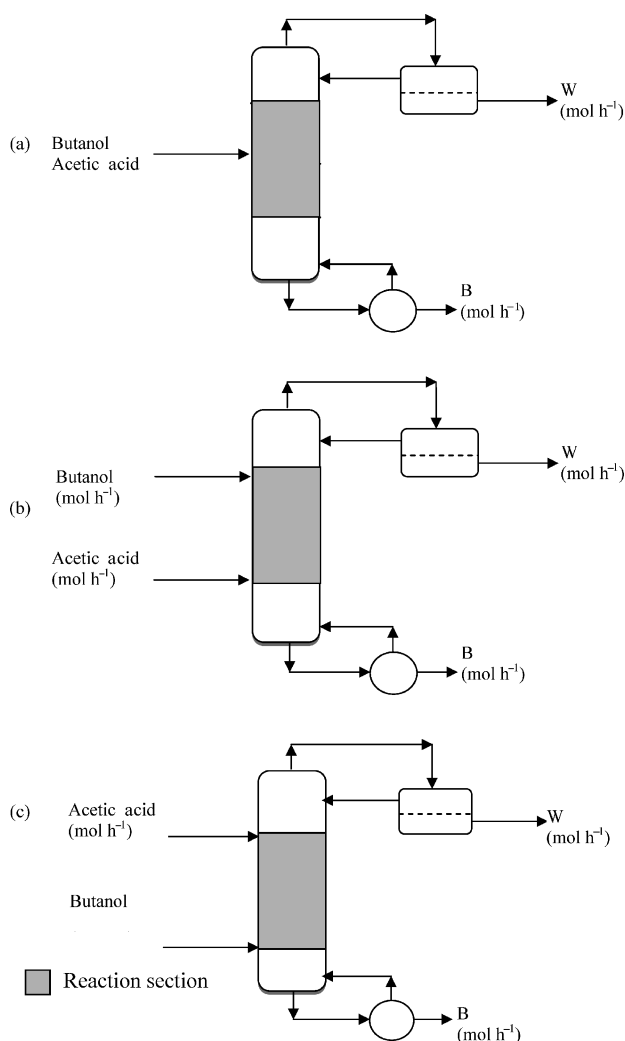

F i g . 2 − *Schematic representation of three different column configurations a) FC, b) SC, c) TC, where W and B refer to flow rates of discarded water and bottom product, respectively.*

The process of reactive distillation was first analyzed with one feed, formed by butanol and acetic acid (FC). This feed was introduced to the middle of the column for different molar ratios, feed flow rates and amount of catalyst. In the other column configurations, the reactants, butanol and acetic acid, were fed into the column separately. Firstly, butanol and acetic acid was fed to the top and bot-

tom of the column, respectively (SC). Then butanol and acetic acid was fed to the bottom and top of the column, respectively (TC).

The operating conditions, purity of butyl acetate and conversion of acetic acid are shown in Table 4 for three different column configurations. As shown in Table 4, purity of butyl acetate increased from 82.5 % to 83.2 % when butanol and acetic acid were fed into the column separately. The counter current operation was preferred to co-current operation when butanol is fed near the bottom of the column. The highest conversion of acetic acid was obtained for third column configuration at a feed flow rate of 1.6 mol h^{-1} and a molar ratio of butanol to acetic acid of 2. Butanol forms minimum boiling azeotropes with water and butyl acetate, so butanol has a volatile character compared to acetic acid. Therefore, feeding of butanol at the bottom of the column is preferable because of its volatility. In all runs, the top product is the mixture of butanol, butyl acetate, water and small amount of acetic acid. Organic phase was separated from water by using a decanter and then water was discarded.

T a b l e   4 – *Results of some reactive distillation experiments*

	FC	SC	TC
F_{AcAc}/mol h^{-1}	1.6	1.6	2.6
BuOH/AcAc	2	2	2
m$_{cat}$/g	50	50	50
x_{AcAc}	0.71	1.7	0.1
x_{BuOH}	16.8	16.7	16.6
x_{BuAc}	82.5	81.6	83.2
Conversion/%	83.0	82.6	84.5

Effect of total feed flow rate

In a catalytic reactive distillation operation, optimization of residence time of reactants is required, and residence time for the reactive zone is related to the flow rates of acetic acid and butanol. For third column configuration, three different experiments were carried out to investigate the effect of feed flow rate at a catalyst amount of 50 g and molar ratio of 2. Fig. 3 shows the effect of feed flow rate on purity of butyl acetate and conversion of acetic acid, respectively. A reduction in acetic acid conversion and butyl acetate purity was observed when the total feed flow rate increased from 1.6 to 2.5 mol h^{-1}. Better results were obtained at lower flow rates due to the sufficient residence time in the reactive zone. As the flow rate was increased, conversion decreased indicating that the system oper-
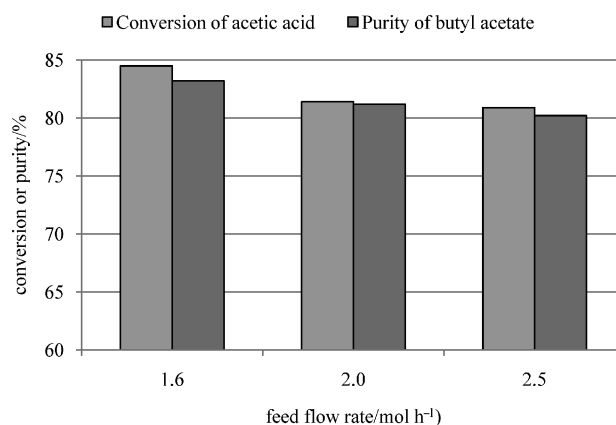

F i g . 3 – *Effect of feed flow rate on the column butyl acetate purity and acetic acid conversion*

ated in the kinetically controlled regime. Similarly, Singh et al.[16] studied the esterification reactions in reactive distillation column at a feed flow rate range of 8.3–24.7 mol h^{-1}. Although the conversion and purity levels in each flow rate were high, better results were observed at lower feed flow rates.

Effect of molar ratio of butanol to acetic acid

Effect of molar ratio of butanol to acetic acid was studied. The excess of butanol was introduced in the column and the molar ratio of butanol to acetic acid was varied from 1 to 2. For third column configuration, three different experiments were carried out to investigate the effect of molar ratio of butanol to acetic acid at a catalyst amount of 50 g and feed flow rate of 1.6. Fig. 4 shows the effect of molar ratio of butanol to acetic acid on the conversion of acetic acid and purity of butyl acetate. The excess of butanol in the reactive zone favored high butanol conversion and butyl acetate purity. The conversion of acetic acid and purity of butyl acetate increased from 81 % to 84.5 %, and 80.5 % to 83.2 %, respectively when the molar ratio of butanol
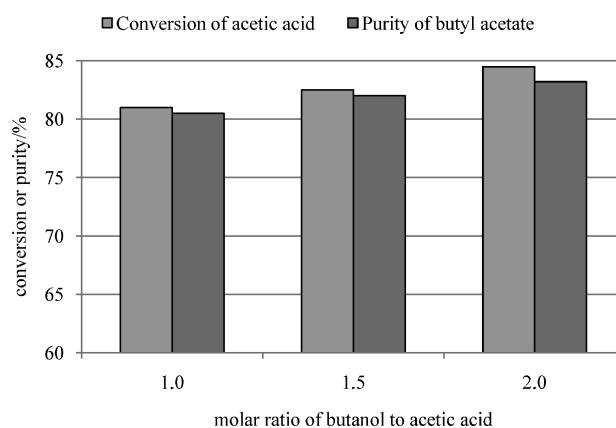

F i g . 4 – *Effect of molar ratio of butanol to acetic acid on the butyl acetate purity and acetic acid conversion*

to acetic acid was increased from 1 to 2. Surprisingly, Singh *et al.*[16] found the reduction in conversion of acetic acid and purity of butyl acetate when molar ratio of butanol to acetic acid had been increased. At higher molar ratios of butanol to acetic acid, dibutyl ether was formed as a side product. This may come from high catalyst loading or high temperature.

Effect of catalyst amount

The amount of catalyst, Amberlyst 15, is another parameter that affects the reactive distillation operation. Some experiments were carried out at three different catalyst amounts, namely, 50 g, 35 g and 25 g. For the third column configuration, as shown in Fig. 5, as the amount of catalyst was increased from 25 g to 50 g, conversion of acetic acid and purity of butyl acetate increased by 2.1 % and 1 %, respectively. Though conversion of acetic acid and purity of butyl acetate increased as the catalyst loading increased, 25 g of catalyst is sufficient for the esterification of butanol with acetic acid. However, in the study of Gangadwala *et al.*,[17] as the amount of catalyst was increased, the purity of butyl acetate decreased due to the formation of by product, dibutyl ether (DBE).
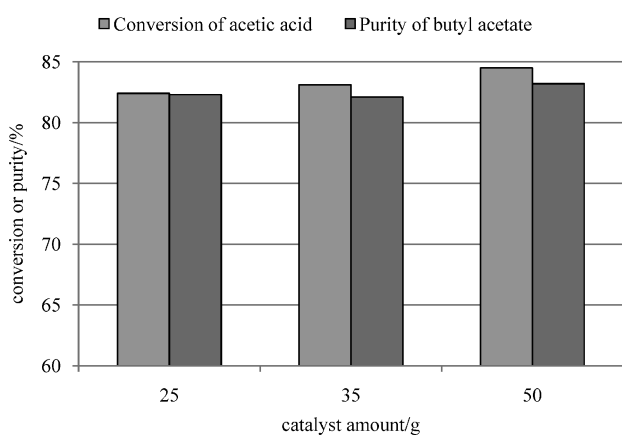

F i g . 5 − *Effect of catalyst amount on the butyl acetate purity and acetic acid conversion*

Effect of reboiler duty

In the esterification of butanol with acetic acid, the reflux ratio is decided by the relative proportion of organic phase and aqueous phase in the top product and it is not a variable. The only operating variable that can make significant impact on the separation and reaction is the reboiler duty. Hence, it was decided to study the effect of reboiler duty on conversion of acetic acid and purity of butyl acetate. The reboiler duty depends on the reboiler temperature; high reboiler duty is obtained at high temperatures. For that reason, in this study, the temperature
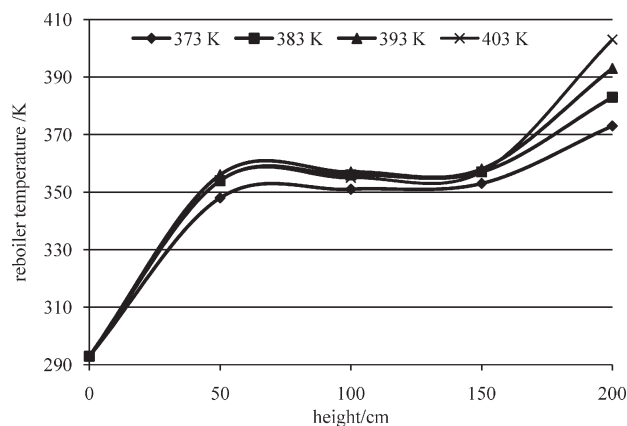

F i g . 6 − *Effect of reboiler temperature on the reactive zone temperature*

in reboiler was raised from 373 K to 403 K to increase the reboiler duty. Fig. 6 shows how temperature of the reactive zone changed when the temperature of the reboiler was changed at a flow rate of 2.5 mol h^{-1} and a molar ratio of butanol to acetic acid of 2. As the reboiler temperature was increased, temperature of reactive zone also increased; however the increment in reaction zone temperature was not significant. The effect of reboiler temperature on purity of butyl acetate and conversion of acetic acid is shown in Fig. 7. There is no significant effect of reboiler temperature on purity of butyl acetate and conversion of acetic acid above 373 K.
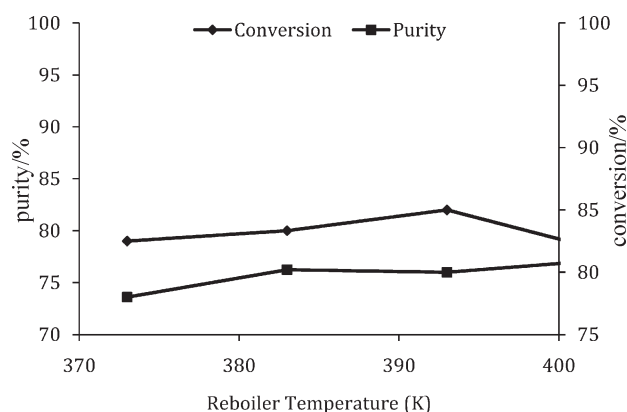

F i g . 7 − *Effect of reboiler temperature on the butyl acetate purity and acetic acid conversion*

Conclusion

The production of butyl acetate by the esterification of acetic acid with butanol was studied in a reactive distillation column using Amberlyst 15 as catalyst. The effect of some operating parameters such as column configuration, feed flow rate, molar ratio of butanol to acetic acid, catalyst amount and reboiler temperature were studied experimentally.

From the experimental studies, the optimum operating conditions of the reactive distillation column for the production of butyl acetate were determined.

The experimental studies show that reactive distillation operation for the esterification of acetic acid with butanol is more effective for the third column configuration than for the other configurations. The high purity butyl acetate and conversion of acetic acid can be obtained by feeding butanol and acetic acid at the bottom and top of the column, respectively.

The total flow rate of 1.6 mol h^{-1} of reactant was chosen as an optimum feed flow rate to provide sufficient residence time in the column.

It was found that the higher molar ratio of butanol to acetic acid resulted in higher acetic acid conversion and butyl acetate purity. However, at high molar ratios, escaping butanol with aqueous phase increased, so the optimum molar ratio of butanol to acetic acid can be selected as 1.

ACKNOWLEDGEMENT

Notations

T – temperature, K

a_i – activity of component i

K_i – adsorption coefficient of component i

K – overall reaction equilibrium constant

F_i – flow rate of component i, mol h^{-1}

m_{cat} – amount of catalyst, g

x_i – mole fraction of component i

W – flowrate of discarded water, mol h^{-1}

B – flow rate of bottom product, mol h^{-1}

Abbreviations

AcAc – acetic acid

BuOH – butanol

BuAc – butyl acetate

FC   – first column configuration

SC   – second column configuration

TC   – third column configuration

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