



Process Systems Engineering and Process Safety

Optimization of coproduction of ethyl acetate and *n*-butyl acetate by reactive distillation[☆]

Hui Tian^{1,*}, Suying Zhao², Huidong Zheng², Zhixian Huang²¹ College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, China² College of Chemistry and Chemical Engineering, Fuzhou University, Fuzhou 350108, China

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ABSTRACT

Based on a previous investigation, a simulation model was used for optimization of coproduction of ethyl acetate and *n*-butyl acetate by reactive distillation. An experimental setup was established to verify the simulated results. The effects of various operating variables, such as ethanol feed location, acetic acid feed location, feed stage of reaction mixture of acetic acid and *n*-butanol, reflux ratio of ethyl acetate reactive distillation column, and distillate to feed ratio of *n*-butyl acetate column, on the ethanol/*n*-butanol conversions, ethyl acetate/*n*-butyl acetate purity, and energy consumption were investigated. The optimal results in the simulation study are as follows: ethanol feed location, 15th stage; acetic acid feed location, eighth stage; feed location of reaction mixture of acetic acid and *n*-butanol, eighth stage; reflux ratio of ethyl acetate reactive distillation column, 2.0; and distillate to feed ratio of *n*-butyl acetate, 0.6.

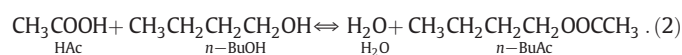
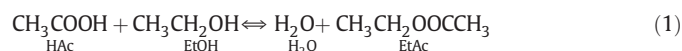
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1. Introduction

Ethyl acetate (EtAc) and *n*-butyl acetate (*n*-BuAc) are common solvents. They are widely used in areas such as lacquering and coating, and many reports on their production have been published [1–8]. Hanika *et al.* [7] studied *n*-BuAc synthesis experimentally using reactive distillation (RD) in a packed column and performed computer simulations to evaluate the experimental data. Three columns were used to obtain high-purity (>99%) *n*-BuAc and the reactive distillation column had 50 theoretical stages. *n*-BuAc (>96%) was obtained using only one reactive distillation column with 26 theoretical stages; a high-purity product (>99%) was obtained by simple separation from the raw product, significantly reducing the energy used. Gangadwala *et al.* [9] explored various reactive distillation configurations for the production of *n*-BuAc to eliminate dibutyl ether byproduct, but did not validate the model results experimentally. Jimenez and Costa-Lopez [10] used methyl acetate and *n*-butanol (*n*-BuOH) to produce *n*-BuAc and methanol; three columns were used to obtain high-purity *n*-BuAc and the reactive distillation column had 43 theoretical stages. Calvar and Gonzalez [11] investigated the reaction kinetics for the esterification of acetic acid

(HAc) with ethanol (EtOH), catalyzed homogeneously by HAc and heterogeneously by Amberlyst 15. A packed-bed reactive distillation column filled with Amberlyst 15 was used to obtain EtAc. The influence of feed composition and reflux ratio was analyzed. Smejkal and Kolena [12] used a complex two-column system consisting of one reactive distillation column (10 trays for reaction plus structured packing for separation) and a downstream stripper, with a decanter in between, to produce high-purity EtAc.

In industry, EtAc and *n*-BuAc are usually produced by the reaction of EtOH and *n*-BuOH with HAc,



In our preliminary study [13], the feasibility of coproduction of EtAc and *n*-BuAc by reactive distillation was investigated and the system as shown in Fig. 1 was proposed. Reactive distillation column I was used to synthesize EtAc. The overhead vapor products were azeotropic mixture of EtAc–H₂O–EtOH, EtAc–H₂O, and H₂O–EtOH, while excess

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* Corresponding author.

E-mail address: 783997@163.com (H. Tian).

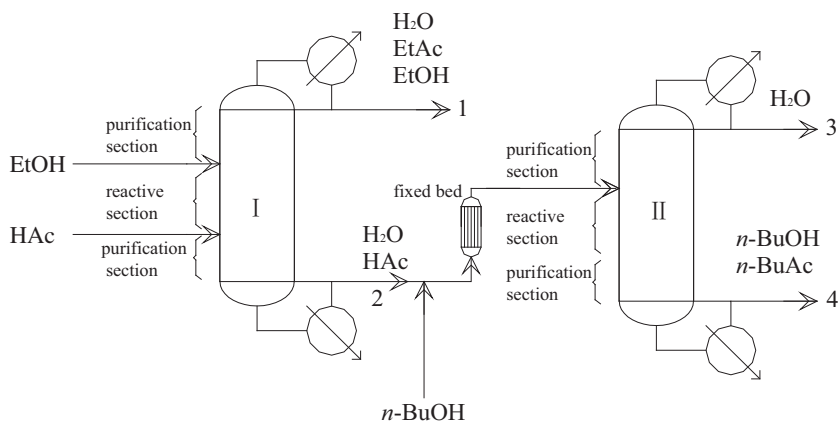


Fig. 1. Flow diagram of EtAc and *n*-BuAc coproduction. I: EtAc reactive distillation column; II: *n*-BuAc reactive distillation column.

HAc, the high boiling-point product, was the bottom product. The bottom product in column I was mixed with *n*-BuOH and introduced to the fixed bed. The water formed by the reaction and brought by HAc was removed from the top product and the organic phase was refluxed back to column II. EtAc and *n*-BuAc outputs were adjusted by changing the molar feed ratio of EtOH to *n*-BuOH in the coproduction procedure, and the HAc purification column used in the separate production process was eliminated. At the feed molar ratio of EtOH to *n*-BuOH of 0.5, 20.4% energy-saving was achieved compared with the separate procedures. The total annual costs of the individual and coproduction procedures were calculated. The total cost of coproduction is 3795912 USD per year less than that of separate processes, 5190921 USD per year, for production of 10000 t of EtAc and 26363 t of *n*-BuAc.

Based on the preliminary study, we perform experimental study for coproduction of EtAc and *n*-BuAc by reactive distillation to verify the model. Emphasis is on using the simulation model to analyze the effects of key parameters such as EtOH feed location, HAc feed location, feed stage of reaction mixture of HAc and *n*-BuOH, reflux ratio of EtAc reactive distillation column, and distillate to feed ratio of *n*-BuAc column on conversions of EtOH/*n*-BuOH, EtAc/*n*-BuAc purity, and energy consumption.

2. Experimental

The coproduction experimental setup is shown in Fig. 1. The reactive distillation columns I and II had the same configurations, with inner diameters of 32 mm, a strong cation-exchange resin (Amberlyst 36Wet) as the catalyst, and parameters given in Table 1. The temperature in the fixed-bed was maintained at 358.15 K. The effluent from the fixed-bed reactor, which almost achieved the chemical equilibrium, entered the reactive distillation column II above the reactive zone. The

reboiler of the reactive distillation column was heated using an electric heating stick and the heating power was measured directly. From the top of the column to the reaction section was the rectifying section, and the stripping section was from the reboiler to the reaction section. The rectifying and stripping sections of the reactive distillation column were packed with bulk θ packing (Φ , 2.5 mm \times 2.5 mm), and catalyst bundles [14,15] containing cation-exchange resin were packed in the middle of the column as shown in Fig. 2, which was the reaction section. The heights of the rectifying, reaction, and stripping sections were 500, 1050, and 650 mm, respectively. To describe the separation efficiency of reactive distillation column quantitatively, the number of theoretical stages of reactive distillation column was estimated, using the Fenske equation, by separating a mixture of EtOH and isopropyl alcohol [16]. The results indicated that the separation efficiencies of the rectifying, reaction, and stripping sections were equivalent to seven, six, and nine theoretical stages, respectively. The theoretical stages were numbered from the top to the bottom in the column. The temperature was measured at eight points in the reactive column while the samples were taken from the top, bottom and along the column (as shown in Fig. 3). The relationship between sampling and number of theoretical stages is shown in Table 2. The temperature was measured by thermocouple and the vapor phase was extracted from the column by a pipe and collected by a small vessel.

Experiments were conducted to evaluate the coproduction technology. The product purity and energy consumption were determined. The temperature at eight points along the column was recorded every half an hour and the composition of sample taken from the top and bottom of the reactive distillation column was analyzed. When the composition of sample taken from the top of the reactive distillation column

Table 1
Physical properties of Amberlyst 36Wet

Properties	
Physical form	Opaque beads
Ionic form as shipped	Hydrogen
Concentration of acid sites	$\geq 1.95 \text{ eq} \cdot \text{L}^{-1}$ $\geq 5.4 \text{ eq} \cdot \text{kg}^{-1}$
Moisture holding capacity	51% to 57% (H^+ form)
Shipping mass	$800 \text{ g} \cdot \text{L}^{-1}$ (50 lbs. ft ³)
Fines content	<0.425 mm: 0.5% max
Coarse beads	>1.180 mm: 4.0% max
Surface area	$33 \text{ m}^2 \cdot \text{g}^{-1}$
Average pore diameter	24 nm
Maximum operating temperature	150 °C (300 °F)

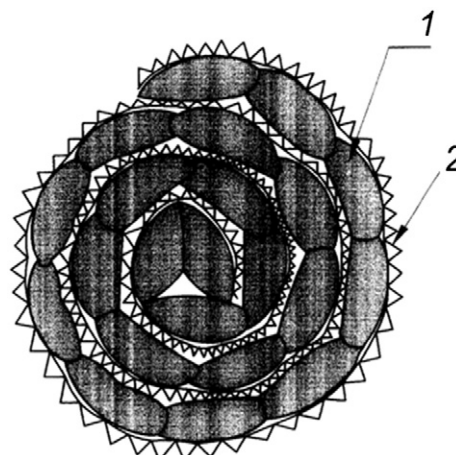


Fig. 2. The schematic diagram of catalyst bundle (1—small bag; 2—ripple silk screen).

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