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Energy efficiency of acetone, butanol, and ethanol (ABE) recovery by heat-integrated distillation

Victor Hugo Grisales Diaz^{1*} and Gerard Olivar Tost²

¹School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

²Faculty of Engineering and Architecture. Department of Electrical, Electronics and Computation Engineering. Universidad Nacional de Colombia – Sede Manizales, Cra. 27 No. 64-60, Manizales, Colombia.

Author information

Corresponding Author

*E-mail: Victor.Grisales-Diaz@newcastle.ac.uk; victor.grisales.d@gmail.com.

Tel.:+ 573008720595

Abstract

Acetone, butanol, and ethanol (ABE) is an alternative biofuel. However, the energy requirement of ABE recovery by distillation is considered elevated (>15.2 MJ fuel/Kg-ABE), due to the low concentration of ABE from fermentation broths (between 15 and 30 g/l). In this work, in order to reduce the energy requirements of ABE recovery, four processes of heat-integrated distillation were proposed. The energy requirements and economic evaluations were performed using the fermentation broths of several biocatalysts. Energy requirements of the processes with four distillation columns and three distillation columns were similar (between 7.7 and 11.7 MJ fuel/kg-ABE). Double-effect system (DED) with four columns was the most economical process (0.12-0.16 \$/kg-ABE). ABE recovery from dilute solutions by DED achieved energy requirements between 6.1 and 8.7 MJ fuel/kg-ABE. Vapor compression distillation (VCD) reached the lowest energy consumptions (between 4.7 and 7.3 MJ fuel/kg-ABE). Energy requirements for ABE recovery DED and VCD were lower than that for integrated reactors. The energy requirements of ABE production were between 1.3- and 2.0-fold higher than that for alternative biofuels (ethanol or isobutanol). However, the energy efficiency of ABE production was equivalent than that for ethanol and isobutanol (between 0.71 and 0.76) because of hydrogen production in ABE fermentation.

Keywords: Biofuel; Distillation; Energy; Process Design; Economic Evaluation

Nomenclature

ABE, acetone, butanol, and ethanol

DE, double-effect

F_{ABE} , production flow of ABE [kg/h]

H_s is the energy consumption of the separation [MJ/kg-ABE]

IRC, investment cost of recovery [\$/kg-ABE]

LHV, lower heating value of solvents [MJ/kg-ABE]

M&S, Marshall and Swift equipment cost index

ORC, operational cost of recovery [\$/kg-ABE]

R_s , the ABE yield [g-ABE/g-substrate]

TRC, total recovery cost [\$/kg-ABE]

TIC, the total investment cost [\$/]

TOAC, the total operational annualized cost [\$/year]

t_{ri} , payback period [year]

t_a , annual operation time [h]

VC, vapor compression

VLE, vapor-liquid equilibrium

3DC, three distillation columns

3DC-VC, three distillation columns with vapor compression

4DC, three distillation columns

4DC-DE, four distillation columns with double-effect

5DC, five distillation columns

Introduction

During the last years, biotechnological production of butanol has been renewed due to its biofuel potential [1]. The biotechnological production is traditionally performed by mesophilic solvent-producing strains [2], such as *Clostridium acetobutylicum*, *Clostridium beijerinckii*, *Clostridium saccharobutylicum* or *Clostridium saccharoperbutylicum*. These biocatalysts produce acetone, butanol and ethanol (ABE). In the Chinese industrial process, ABE is produced in the average ratio of 2.5:4.8:1 (calculated from stoichiometric reaction reported by Ni and Sun [3]). The main advantage of traditional *Clostridium* is the ability to consume a wide variety of substrates, such as glucose, sucrose, lactose, xylose, starch and glycerol [4].

To achieve a high conversion avoiding product inhibition, the substrate is fed at low concentration (55-75 g/l) into the reactor. This characteristic makes steam consuming operations, such as mash sterilization, downstream product recovery and wastewater treatment energy demanding [5]. In order to reduce water usage for biobutanol production [3], vinasses from distillation in Chinese industry are recycled into the reactor in ~40%.

Integrated reactors with separation units have been proposed to reduce energy requirements, investment cost and vinasses production [6–10]. Qureshi et al. [6] reported that liquid-liquid extraction and adsorption processes have the lowest energy requirements with 8.9 and 8.2 MJ/kg-butanol, respectively. In another study, pervaporation (9 MJ/kg-ABE) and liquid-liquid extraction (14 MJ/Kg-ABE) were the integrated systems with the lowest energy requirements [11].

Final purification of integrated and conventional reactors for biobutanol production is traditionally carried out by distillation. These distillation systems have conventionally five stages. In the first column, ABE is concentrated at 60 wt%. Acetone and ethanol are concentrated in two columns, while butanol and water are concentrated finally in an azeotropic distillation system of two columns. In azeotropic distillation, decantation is used to break the azeotropic behavior of butanol and water [12]. A separation agent for decantation is not needed because butanol is partially miscible in water.

A great steam consumption (13-25 kg-steam/kg-ABE) have been reported in Chinese industrial processes [3]. In academic evaluations of distillation processes, based on industrial processes, high-energy requirements have been reported commonly (24.2 MJ/kg-butanol [6] or

28 MJ/kg-butanol [13]). However, Jilin Cathy Industrial Biotech recently reported a low energy requirement of distillation system of 6-7 kg-steam/kg-butanol [14]. The reasons for the differences in the energy requirements are undefined.

Distillation can be integrated to reduce its energy requirement. Process integration in distillation follows various routes such as: internal heat integrated distillation columns [15, 16], vapor compression (VC) distillation [17, 18], petlyuk or dividing wall columns [19], double-effect (DE) distillation [20, 21] and cyclic distillation [22, 23]. Among these alternatives, Kaufman et al. [17] proposed a sequential system of multiple VC for ABE recovery (patented process). Additionally, low energy requirements have reported in our previous work with DE (7.2 MJ/kg-ABE) [24].

In this paper, four heat-integrated distillation systems were evaluated energetically. Integrated distillation systems may need an investment higher than that for conventional distillation; therefore, an economic analysis was performed. Considering biofuel application, the energy efficiency of ABE recovery by distillation was compared with that for the dehydration of alternative biofuels (isobutanol, ethanol and isopropanol, butanol and ethanol (IBE) [25, 26]). Due to its high-energy efficiency (between 0.71 and 0.76), the distillation systems studied in this work will provide a new baseline of energy requirements.

Methods

The simulations were performed in Aspen Plus®. RadFrac was the unity used for distillation simulation. Trays selection was sieve's type. Pressure drop in the column was calculated with tray rating of RadFrac. The base method in simulations was UNIQUAC-RK with CO₂ and H₂ as Henry's components.

The accuracy of UNIQUAC or NRTL liquid-liquid equilibrium (experimental data [27, 28]) using the binary parameters of vapor-liquid equilibrium (VLE) is very low (Fig. 1). Therefore, the binary parameters of the decanter units must be different to the distillation units. The binary parameters of distillation were APV73 LLE-ASPEN (Fig. 1). The parameters for butanol-water mixture were those reported by Fisher and Gmehling [13, 29]

In all the distillation systems studied in this work, condensation heat was not used to preheat the feed of ABE concentration columns. Instead, the exit from these distillation columns was used to preheat their respective feed, maximizing the heat integration [25]. The distillation

processes after this integration achieved a waste mash temperature of 47 °C (fermentation temperature of 37 °C, minimum approach temperature of 10 °C), which is a temperature suitable for solids concentration by filtration [30].

Butanol boiling point is high (117 °C). However, the azeotrope of minimum boiling point of butanol and water increased the relative volatility of butanol at low concentrations. Indeed, butanol has a relative volatility at low concentrations in water 2.3-fold higher than ethanol. Consequently, butanol in all processes is recovered from the top of C1 column. Vinasses were partially recycled to the reactor to reduce the substrate concentration (18 wt%) and water requirements [3].

System with four distillation columns (4DC)

ABE in the 4DC process was separated sequentially based on its boiling point (Fig. 2). Therefore, acetone, ethanol, and butanol were obtained in the columns C2, C3, and C4, respectively. Due to butanol-water azeotrope, the top stream of C1 is not anhydrous. In this work, the concentration of water at the top of C1 was reduced with a decanter (Fig. 2). The reflux of C1 was the aqueous phase from decanter (Fig. 2). The organic phase from the decanter was the stream fed to C2. In this way, the water concentration (~37 wt%) of organic phase of the decanter depends mainly on the temperature of the decanter. An additional reflux was not required. Ethanol and acetone were purified at the top of C2 and C3, respectively. While, the bottoms were fed at their respective decanter (Fig. 2). Therefore, three decanters were used. These decanters reduced the water concentration because the polar components, acetone and ethanol, were recovered sequentially.

The binary azeotrope of butanol-water was broken in the decanter between the columns C3 and C4 (Fig. 2). The temperature of decanters was fixed at 40 °C because the distribution coefficient was high at this point (Fig. 1). Butanol was produced in the bottoms of C4. The top of C4 is condensed and recirculated to the decanter. The feed of C4 from the decanter was at the top stage. For this reason, an additional reflux was not required. Conventionally, ABE is purified using five distillation columns (5DC). In 5DC, the aqueous phase from the decanter is fed to a fifth column. However, in this work to reduce the number of columns the aqueous phase was recycled to C1 (Fig. 2). The Fig. 3 shows the composition profiles for each distillation column of 4DC system.

The condensation heat of columns at atmospheric pressure or higher may be used in the boiler of another column if it operates at low-pressure. Low-pressure columns (C2, C3, and C4) were proposed to use the heat of condensation of C1 column in their respective boilers. The exchanger area of condensation and the diameter of columns increase a lower pressure of operation. However, this effect is not necessary true in the acetone column (C2), due to the increase of acetone volatility at low pressures [31–33] (Fig. 4). The total stage numbers of all columns and processes are shown in Table 1. The total stage numbers of 4DC were 90. In all cases, the total stages were chosen to avoid an excess of trays.

System with three distillation columns (3DC)

Total stages in the configuration with three distillation columns (3DC) were reduced from 90 to 70 (Table 1). In the first column (C1), acetone and ethanol were obtained mainly at the top stage (Fig. 5). A side stream from C1 was fed to the decanter (Fig. 5). The organic phase, (~68 wt% of butanol and ~24% of water), was fed to butanol column (C3) and the aqueous phase was recycled to C1. Acetone and ethanol were purified simultaneously in C2. Butanol was purified in C3. The top of C3 was condensed and fed to the decanter to break the butanol-water azeotrope.

Similar to 4DC, low-pressure operation were proposed for C2 and C3 columns. Butanol was not present at the top of C1, making the condensation temperature at the top of this column low (62 °C). Consequently, heat integration using this heat of condensation is difficult. For this reason, intermediate condensation in C1 (stage 15) was used to apply its heat in C2 and C3 boilers (Fig. 5).

Three distillation columns and vapor compression (3DC-VC)

3DC-VC is shown in Fig. 6. The configuration of streams in 3DC-VC was different to 3DC. In C1 column, one side stream was not used and the vapor on top of C1 column was split into two streams. One stream was compressed and another was not. This effect was used to reduce the compression work. The vapor compression was limited due to the high cost of compressors. The condensation heat of compressed stream was applied in the boiler of C1 column. The condenser heat of vapor uncompressed was used in boilers of low-pressure columns (C2 and C3).

In the columns C2 and C3 vapor compression was not considered due to the high-temperature difference between its condenser and boiler (42-45 °C). Acetone was obtained from the top of C2 column. Ethanol was obtained from the top, and butanol was obtained from the bottoms of C3 column. Composition profiles for each distillation column of 3DC-VC system are shown in Fig. 7.

Four distillation columns with double-effect (4DC-DE)

4DC-DE was proposed in our previous study [24]. The stream after fermentation is divided into two streams, then preheated and fed to columns C1-HP and C1-LP (Fig. 8). In this system, columns C1 (1.1 bar) and C3 (1.2 bar) operated at a pressure moderately higher than atmospheric pressure to improve the heat integration. Due to butanol and water azeotrope, C3 has no-condenser and the steam from the top of C3 is fed directly to C1-HP to reduce their energy requirements. The heat of a side condenser in column C1 was used to apply its condensation heat to the boiler of low-pressure columns (C1-LP (0.3 bar) and C2 (0.5 bar)). The split ratio of the stream after fermentation was iterated until the sum between condensation heat of C1 (Q_{1A}) and boiler heat of C1-LP (Q_{1B}) and C2 (Q_2) become nil (Fig. 8). The total energy consumption of 4DC was given by the steam requirements of columns C1 and C3.

Energy and economic evaluation

In this work, the energy requirements were reported in two different units: the sizing units of heat exchangers that does not necessarily required steam from furnace are reported in the units “MJ/kg-ABE” (Table 2), while the units of fuel requirements of heat exchangers and compressors are “MJ fuel/kg-ABE” [24] (Table 3). The units “MJ fuel” of the units that required vapor and electricity are calculated assuming efficiencies of 0.9 and 0.33, respectively [24]. CO₂ production is proportional to fuel combustion. Therefore, a reduction in fuel requirement is proportional to CO₂ reduction. Heat integration was performed with 10 °C of minimum approach temperature. Compressor efficiency was 0.75.

Configurations were evaluated using dilute solutions with the ABE yield of Chinese industrial. Butanol concentration in the reactor was assumed as 10 g/l (base case). Additionally, ABE recovery from dilute solution produced by three hyper-butanol mutant strain was studied. The butanol concentration in the reactor of all cases evaluated are reported in Table 3. The ABE and hydrogen yield of microorganism processes were calculated using the theoretical yield of

stoichiometric reactions and the specific conversions. In this work, biomass and other sub-products of low yield in the fermentation, e.g. acetic acid, and high boiling point were not included in the estimation. Glucose conversion in the stoichiometric reactor was 0.83. The specific glucose conversions to butanol, ethanol and acetone are estimated from the A:B:E ratio reported in Table 3. The stoichiometric reactions for butanol or isobutanol, acetone and ethanol production are:



In all simulations, the purities (mass fraction) of butanol, acetone, and ethanol were 0.997, 0.99, and 0.89, respectively. Non-condensable products were compressed and recycled to the stripping column (10 stages). Cooling water (10000 kg/h) was used in the stripping column to recover solvents from the non-condensable stream. The production of anhydrous ethanol, isobutanol and IBE were not carried out in this study. The recovery cost per kg of product (TRC) was calculated from:

$$TRC = ICR + OCR \quad (4)$$

$$ICR = \frac{TIC}{t_{ri} \cdot F_{ABE} \cdot t_a} \quad (5)$$

$$OCR = \frac{TOAC}{F_{ABE} \cdot t_a} \quad (6)$$

where F_{ABE} is the production flow (kg-ABE/h), t_{ri} is the payback period (three years), t_a is the annual operation time (8150 h/y), TOAC is the total operational annualized cost (\$/y), TIC is total investment cost (\$), IRC is the investment cost of recovery (\$/kg-ABE) and ORC is the operational cost of recovery (\$/kg-ABE). Equipment cost was calculated with functions reported by Douglas [34]. Costs of steam, cooling water, and electricity and Marshall and Swift equipment cost index (M&S) were assumed as 16 \$/ton, 0.006 \$/kg and 0.126 \$/kWh and 1625 (dimensionless), respectively. The production capacity of solvents was 5000 kg-ABE/h. Process equipment was designed using stainless steel material. Ideal energy efficiency of separation (IES) system was calculated as proposed [25] using:

$$IES = \frac{R_s \cdot (LHV - H_s)}{LHV_{Glucose}} \quad (7)$$

Where, LHV is the lower heating value of solvents and hydrogen (MJ fuel/kg-solvent), H_s is the energy consumption of the separation (MJ fuel/kg-solvent), and $LHV_{GLUCOSE}$ is the lower heating value of glucose (16.45 MJ/kg [35]). The energy efficiency was considered ideal because was not calculated the energy requirement of pretreatment and downstream. The yield (R_s) was the mass of ABE recovery per mass of substrate consumed.

Results

The distillation process with the lowest energy requirements, 3DC-VC, achieved a fuel requirement of 7.3 MJ fuel/kg-ABE (ABE yield and ratio of the Chinese industry, Table 2). The coefficient of performance of the heat-pump was 8.6 (-) (the energy savings (MJ) divided by the compression work (MJ)). 3DC-VC process reduced the fuel requirement in comparison with 3DC by 37 %. Consequently, ORC decreased by 33%. However, the TRC of 3DC-VC was equivalent to that of 3DC (Table 3) due to the high investment cost of the compressors.

The most economical process or with the lowest TRC, 4DC-DE, achieved a fuel requirement of 8.7 MJ fuel/kg-ABE. 4DC-DE reduced the energy requirements of 4DC by 25.6%. Although the energy requirements of 4DC-DE were 1.2-fold higher than that of 3DC-VC, 4DC-DE was the most economical option because the IRC was not increased drastically using this heat integration. For instance, the IRC of 4DC-DE increased only by 1.4% with respect to 3DC, instead of the high number of stages of 4DC-DE (95, Table 1) and the operating pressure of C1-LP (0.2 atm at the top). This low increment of IRC was achieved because 4DC-DE was the distillation system with the lowest total boiler flux (23.9 MJ/kg-ABE, Table 2). Due to the low butanol concentration (~10 g/l), total boiler heat flux was the most important factor in the calculation of IRC. Given that C1-LP was operated to low pressure, the preheating of 4DC-DE was the lowest (Table 2). In the preheating was achieved the biggest heat integration due to the low solvent concentration (20 g-ABE/l), (between 14.9 and 15.1 MJ/kg-ABE, Table 2).

The main difference between 3DC and 4DC configurations was the total boiler heat of the purification columns (C2, C3 and C4), Table 2. The sum of boiler heat of purification columns of 4DC was 3.2 MJ/kg-ABE (Table 2). While with 3DC process, this sum was 1.7-fold lower due to less unnecessary condensation). 4DC-DE and 3DC have the lowest boiler heat of

purification (between 1.5 and 1.9 MJ/kg ABE) because a vapor stream, instead of a liquid stream, was fed to column C2.

Due to heat integration, the fuel consumption of 3DC and 4DC only depended on the boiler heat of column C1. Consequently, the fuel requirements of purification columns were nil and the energy requirements of 4DC and 3DC configurations were equivalents (~11.5 MJ fuel/kg-ABE, Table 3). For this reason, ORC (related to fuel requirements) of both process was similar. ORC was approximately 58% of TRC. Given that the total boiler heat flux of 3DC was 6.2% lower than that of 4DC (Table 2), the IRC of 3DC was 4% lower (Table 3).

The fuel requirements of 4DC-DE with the ratio achieved by *C. acetobutylicum JB200*, *C. beijirinkii BA10*, and *C. acetobutylicum SolRH* were reduced from 8.7 MJ fuel/kg-ABE to 6.3 MJ fuel/kg-ABE, 6.5 MJ fuel/kg-ABE and 6.1 MJ fuel/kg-ABE, respectively (Table 3). This was to be expected because of the high concentration of butanol in the fermentation broth (around 20 g/l). Consequently, the TRC was reduced between 22% and 25% (Table 3). The least energy requirement and TRC were obtained using a hyper-butanol producing *C. acetobutylicum JB200* (Table 3). Due to a higher butanol titer, vinasses recycle into the reactor was reduced from 67% to 56.3% and 34.8% using the yield of *C. beijirinkii BA101* and *C. acetobutylicum JB200* with respect to the base case, respectively.

Vinasses recycle was an important contribution of the low energy requirements achieved in this work. At similar total ABE recovery, vinasses recycle reduced the energy requirements by ~18.8% with respect to 4DC or 3DC process without vinasses recycle (data not shown). This reduction was mainly achieved because ethanol has the lowest relative volatility and ethanol concentration is increased in the reactor with vinasses recycle (results not shown).

Energy efficiency of ABE processes without hydrogen combustion for 3DC-VC and 4DC-DE were between 0.59 and 0.66. Hydrogen production (LHV of hydrogen, Table 4) was between 9 and 15% of total energy produced. Therefore, the efficiency increased to 0.71-0.76 with hydrogen combustion. Energy efficiency of 3DC-VC was between 4.8 and 5.8% higher than that for 4DC-DE. The highest efficiency of the distillation process was achieved using *C. acetobutylicum JB200*. Although *C. beijirinkii BA101* has the lowest theoretical yield of hydrogen, the stoichiometric ABE yield is higher than that of *C. acetobutylicum SolRH*. Hence,

the energy efficiency of *C. beijirinkii* BA101 and *C. acetobutylicum* SolRH was similar (4DC-DE (0.71) and 3DC-VC (0.74-0.75)).

Discussion

In some Chinese industrial processes have been reported high energy requirements, 13-25 kg-steam/kg-ABE [3] or 30-58 MJ fuel/kg-ABE. The minimum energy requirements reported for these processes (30 MJ fuel/kg-ABE) were similar to that of 4DC without heat integration (28.9 MJ/kg-ABE). Hence, in these industrial processes, heat integration probably was not used.

Energy consumption of distillation reported by Jilin Cathy Industrial Biotech is 6-7 kg-steam/kg-butanol [14] (butanol concentration from the fermentation broth is not reported). Assuming an efficiency of steam production of 0.9 and using the ratio of Chinese industry reported by Ni [3], the fuel consumption was between 8-9.4 MJ-fuel/kg-ABE. Based on the low energy consumption reported for this industrial process, a heat-integrated distillation system may have been used. These energy requirements were equal to the fuel consumption achieved for 3DC or 4DC with a butanol titer between 14 and 15 g/l (data not shown).

It is important mention that comparisons between energy requirements of different distillation systems must be done at the same butanol concentration in the feed. This was suggested because it was found that increments of the concentration of butanol from 10 to 20 g/l reduced the energy requirements 1.7 times.

In academy studies of distillation, the energy requirements reported for ABE recovery were 15.2 MJ-fuel/kg-ABE using *C. beijirinkii* BA101 and a distillation system of 5DC (135 ideal stages [5]). The total energy requirements of 3DC-VC and 4DC-DE were respectively 67.1% and 58.6% lower than that of 5DC (Table 2) due to heat integration, vinasses recycle and the high efficiency of the distillation systems studied in this work. In similar way, using the yield of *C. acetobutylicum* SolRH, the energy requirements of 3DC-VC and 3DC were 60% and 38% than that of 5DC (12.6 MJ-fuel/kg-ABE, Table 2), respectively. Remarkably, using 3DC the total number stages of 5DC was reduced from 135 (ideal stages) to 70 (non-ideal stages).

Several energy analysis of integrated reactors have been reported in the literature [6, 11, 13]. From an energy point of view, the most attractive units reported by Qureshi et al. [6] were adsorption, liquid extraction, and pervaporation. Energy requirements of liquid extraction

and adsorption reported by Qureshi et al. [6] for *C. beijerinckii* BA101 are 7.1 and 7.7 MJ fuel/kg-ABE (calculated in this work from *C. beijerinckii* BA101 ratio), respectively. Energy consumption of pervaporation reported by Groot et al. [11] and Qureshi et al. [6] are 10 and 10.9 MJ fuel kg⁻¹ ABE, respectively (assuming an efficiency in energy production of 0.9).

Fuel consumption of 4DC-DE and 3DC-VC achieved in this work were 29.1 and 34.8% and 17.9 and 10.7 % lower than that reported by Qureshi et al. [6], for liquid-liquid extraction and adsorption, respectively. However, an integrated reactor may have a higher productivity of solvents. Hence, an economic study of reaction and purification system is necessary [24]. On the other hand, an integrated reactor is not 100% selective and requires a final purification. For this reason, it can be coupled with the distillation processes studied in this work.

The lowest energy requirement in the literature was achieved with a vapor compression system (membrane assisted vapor stripping (MAVS), 4.2-MJ-fuel/kg-ABE (3/6/1) at 2 wt% of ABE [36, 37]). In the evaluation of MAVS, CO₂ and H₂ were non-included, the minimum approach temperature was 5 °C, the ratio of ABE was 3/6/1, ABE titer was 20 g/l, ethanol recovery was 90% and nil pressure drop was assumed. Using the same assumptions reported by [36, 37], the energy requirement of 3DC-VC were reduced from 7.3 to 4.5 MJ-fuel/kg-ABE. Hence, the low energy requirements of MAVS were mainly achieved through heat integration by vapor compression. A similar result was observed in our previous study for ethanol or isobutanol dehydration [25]. However, it is important to mention that non-condensable, pressure drop, among others, may have a different effect in MAVS and recycle of vinasses are not performed in MAVS.

Due to biofuel application, the IES of ABE process was compared with ethanol, isobutanol and IBE dehydration by heat-integrated distillation (Table 4). IBE anhydrous was achieved in a new approach of heat-integrated distillation [26]. In this simultaneous azeotropic and extractive distillation system, without an additional entrainer, butanol is used to break the azeotropes of isopropanol-water and ethanol-water. In this approach, VC was used. The energy requirements of IBE dehydration are between 1.3- and 1.6-fold lower than that of 3DC-VC (Table 4). For this reason, the energy efficiency of IBE dehydration was the highest (0.79-0.80, Table 4). Although IBE dehydration achieved the highest IES, it is worth noting that the effect of

CO₂, the efficiency of stages, pressure drop and the energy requirements for the end purification of IBE were not studied in our previous work [26].

Ethanol and isobutanol anhydrous (99.7 wt%) are achieved by extractive and azeotropic distillation, respectively [25]. Glycerol is the extractant used in ethanol dehydration system [25]. The concentration of ethanol and isobutanol from broth are 10 and 2 wt% [25], respectively. The TRC of isobutanol purification by VC was 1.07-fold lower than that of ABE purification by 3DC-VC (*C. acetobutylicum JB200*, Table 3). The energy requirements of 3DC-VC were between 1.3 and 2.0-fold higher than that for ethanol and isobutanol dehydration (Table 4). However, due to hydrogen synthesis, the IES of ABE production by 3DC-VC was only between 1.5 and 2.8 % lower than that for ethanol and isobutanol dehydration (Table 4).

Conclusions

Conventionally, distillation is considered an inefficient alternative method for ABE recovery. However, with the configurations investigated in this paper, distillation was an alternative energetically attractive. The energy requirements were between 4.7 and 7.3 MJ fuel/kg-ABE and 6.1 and 8.7 MJ fuel/kg-product using vapor compression distillation and double-effect, respectively. The fuel requirements were reduced between 1.4- and 1.7- fold when the butanol concentration rises from 10 to 20 g/l. The most economical option was double effect distillation with recovery cost between 0.12 and 0.16 \$/kg-product. The lowest energy requirement and the highest efficiency for ABE recovery was achieved with *C. acetobutylicum JB200*. The energy efficiency of ABE recovery was 1.5-2.8% lower than that of isobutanol or ethanol.

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Conflict of interest

The authors declare that no competing interests exist.

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Tables

Table 1 Feed inlet stages and number of stages of the heat-integrated distillation processes studied in this work

Column	Feed inlet stage			
	Distillation system			
	4DC	3CD	3DC-VC	4DC-DE
C1	1-3	21-23	1-3	
C1-LP				1-3
C1-HP				15-21-23
C2	15	14	15	21
C3	12	1	20	1
C4	1			
Number total of stages ^b				
Column	Distillation system			
	4DC	3CD	3DC-VC	4DC-DE
C1	20	40	20	
C1-LP				20
C1-HP				40
C2	30	20	30	25
C3	30	10	30	10
C4	10			
Total	90	70	80	95

^a stages from the top, ^b Murphree tray efficiency of 0.7

Table 2 Boiler heat flux of the ABE distillation systems and the yield of Chinese industry

Column	4DC	3CD	3DC -VC	4DC- DE
C1	10.6	10.3	10.5	-
C1-LP	-	-	-	7.8
C1-HP	-	-	-	2.7
C2	0.91	0.78	1	0.46
C3	1.5	1.1	1.7	1.04
C4	0.83	-	-	-
Preheating of feed from fermentation	15.2	14.9	15.2	12
Total purification (C2-C4)	3.2	1.9	2.7	1.5
Total boiler heat (C1-C4)	13.8	12.1	13.2	11.9
Total heat exchangers	28.9	27.1	28.4	23.9

Table 3 Total recovery cost (TRC) and fuel requirement of ABE recovery by heat-integrated distillation ^a

Biocatalyst	Butanol titer [g/l]	Solvent ratio: A/B/E	System	ABE recovery	Fuel requirement [MJ fuel/kg-ABE]	IRC [\$/kg-ABE]	ORC [\$/kg-ABE]	TRC [\$/kg-ABE]
Typical microorganisms in Chinese industrial process	10	2.5/4.8/1	4DC	0.970	11.7	0.084	0.113	0.197
			3DC	0.969	11.5	0.078	0.111	0.189
			3DC-VCD	0.970	7.3	0.115	0.075	0.190
			4DC-DE	0.969	8.7	0.079	0.080	0.159
<i>C. beijirinkii</i> BA101	19.7 [38]	6/24.6/1	3DC	0.976	7.6	0.064	0.074	0.138
			3DC-VCD	0.977	5.0	0.088	0.052	0.140
			4DC-DE	0.980	6.3	0.064	0.059	0.123
			5DC ^b	-	15.2	-	-	-
<i>C. acetobutylicum</i> SolRH	18.5 [39]	4/8.4/1	3DC	0.977	7.8	0.062	0.076	0.138
			3DC-VCD	0.981	5.0	0.087	0.053	0.140
			4DC-DE	0.977	6.5	0.063	0.061	0.124
			5DC [5] ^b	-	12.6	-	-	-
<i>C. acetobutylicum</i> JB200	20.4 [40]	5/9.2/1	3DC	0.977	7.0	0.059	0.069	0.128
			3DC-VCD	0.976	4.7	0.083	0.050	0.133
			4DC-DE	0.978	6.1	0.062	0.057	0.119
<i>e. coli</i> (isobutanol)	20	-	VCD [25]	0.999	2.5	0.087	0.036	0.124

^a Ethanol dehydration costs and energy recovery for anhydrous ethanol production were not included. ^b Calculated from reference [5].

IRC, investment cost of recovery. ORC, operational cost of recovery.

Table 4 Energy efficiency of biofuels recovery by heat-integrated distillation

Fermentation	Recovery system	Biocatalyst	Yield (kg-solvent/kg-glucose)	Energy recovery (MJ fuel/kg-ABE)	LHV hydrogen (MJ/kg-ABE)	LHV solvents (MJ/kg-ABE)	Efficiency
ABE (In this work)	3DC-VC	<i>C. beijirinkii</i> BA101	0.385	5.0	3.2	33.3	0.74
	3DC-DE		0.385	6.3	3.2	33.3	0.71
	3DC-VC	<i>C. acetobutylicum</i> JB200	0.373	4.7	5.6	32.4	0.76
	3DC-DE		0.373	6.1	5.6	32.4	0.72
	3DC-VC	<i>C. acetobutylicum</i> SolRH	0.374	5.0	5.3	32.5	0.75
	3DC-DE		0.374	6.5	5.3	32.5	0.71
Isobutanol	VC [25]	<i>escherichia coli</i>	0.41	3.7	-	34.4	0.77
	DE [25]		0.41	5.7	-	34.4	0.72
Ethanol	DE [25]	<i>saccharomyces</i>	0.51	3.4	-	27	0.73
	VC [25]	<i>cerevisiae</i>	0.51	2.5	-	27	0.76
IBE	VC [26]	<i>C. acetobutylicum</i> PJC4BK	0.39	2.9	3.9	32.7	0.80
	VC [26]	<i>C. acetobutylicum</i> RH8	0.40	3.7	2.9	33.1	0.79

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Fig. 1

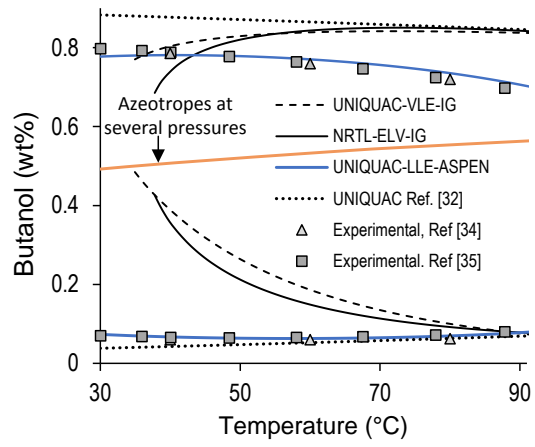


Fig. 2

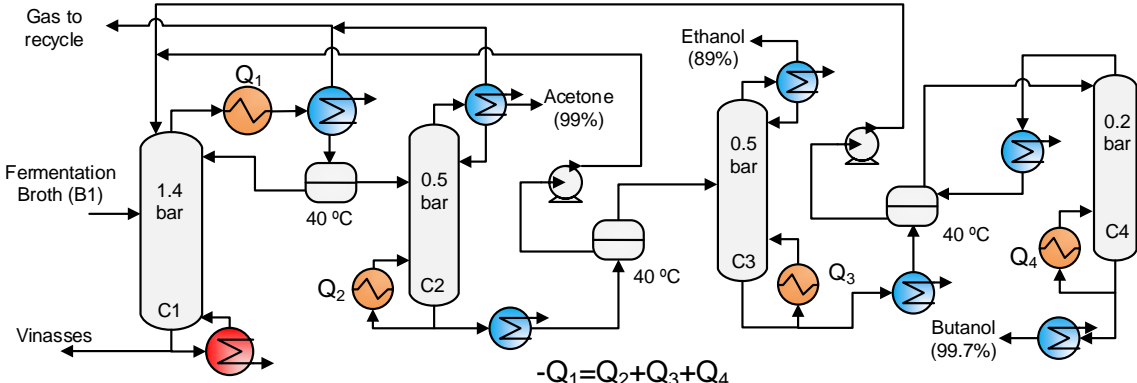


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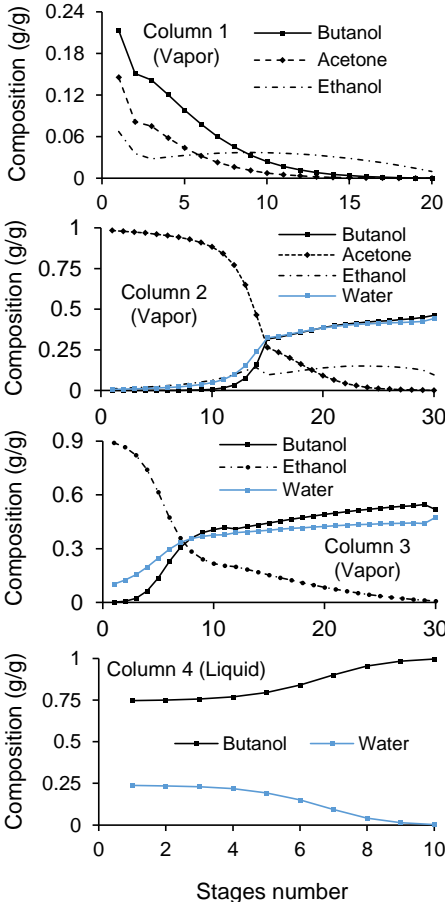


Fig. 4

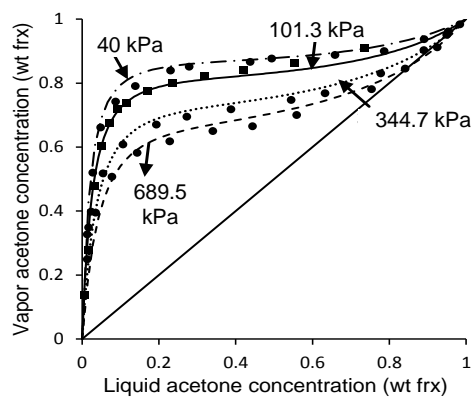


Fig. 5

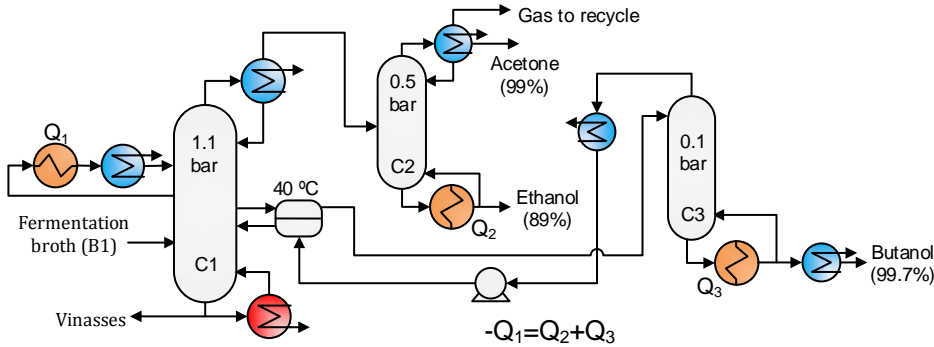


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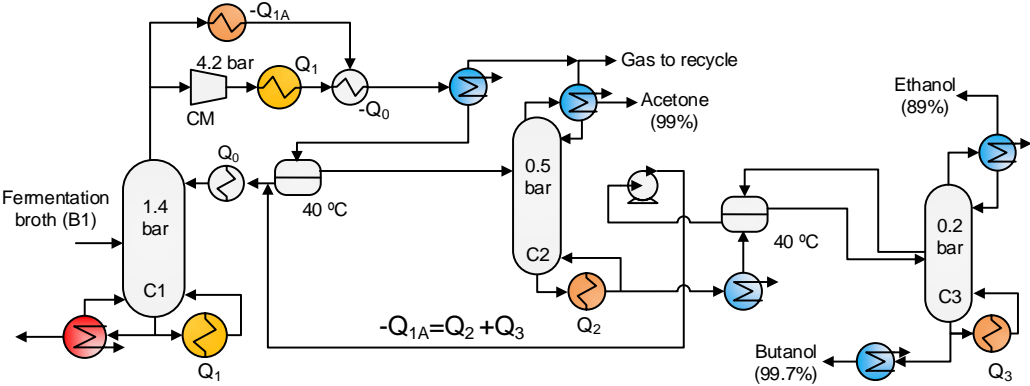


Fig. 7

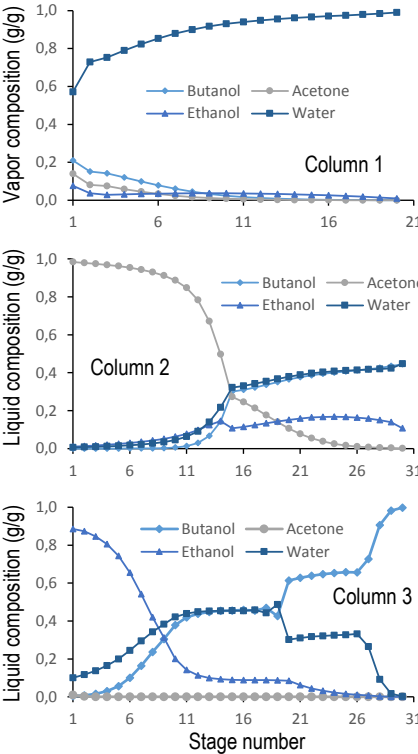


Fig. 8

