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Edited by
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Enhanced Down-Stream Processing of Biobutanol in the ABE Fermentation Process

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Abstract

Butanol is considered a superior biofuel, as it is more energy dense and less hygroscopic than bioethanol, resulting in higher possible blending ratios with gasoline. However, the production cost of the acetone-butanol-ethanol (ABE) fermentation process is high, mainly due to the low butanol titer, yield, and productivity in bioprocesses. The classic recovery by distillation is an energy-intensive process that has largely restricted the economic production of biobutanol. Other methods based on gas stripping, liquid-liquid extraction, adsorption, and membranes are also energy intensive due to the bulk removal of water. This study proposes a novel process for the butanol recovery by enhanced distillation, using only several operating units in an optimized sequence to reduce costs. This work considers a plant capacity of 40 ktpy and purities of 99.4 %wt butanol, 99.4 %wt acetone and 91.4 %wt ethanol. The process was simulated and optimized using Aspen Plus as PSE tool. The enhanced process proposed here is cost effective and can be readily employed at large scale to improve the economics of biobutanol production.

Keywords: ABE fermentation, energy efficiency, distillation, process simulation

1. Introduction

Butanol is an alternative fuel with characteristics similar to petro-fuels. Its production by the ABE fermentation process has received renewed attention, and the developments resulted in higher butanol concentrations, less fermentation by-products and higher volumetric productivities during fermentation (Xue et al., 2013). However, these have to be matched by a down-stream processing that is less energy intensive and can reduce the separation costs (Xue et al., 2013; 2014; Huang et al., 2014; Kiss et al., 2015). In addition to distillation, other methods based on gas stripping, liquid-liquid extraction, adsorption, and membranes were investigated (Kraemer et al., 2010; vd Merwe et al., 2012; Mayank et al., 2013; Errico et al., 2015). This work proposes a new optimized distillation sequence that can radically improve the economics of biobutanol production.

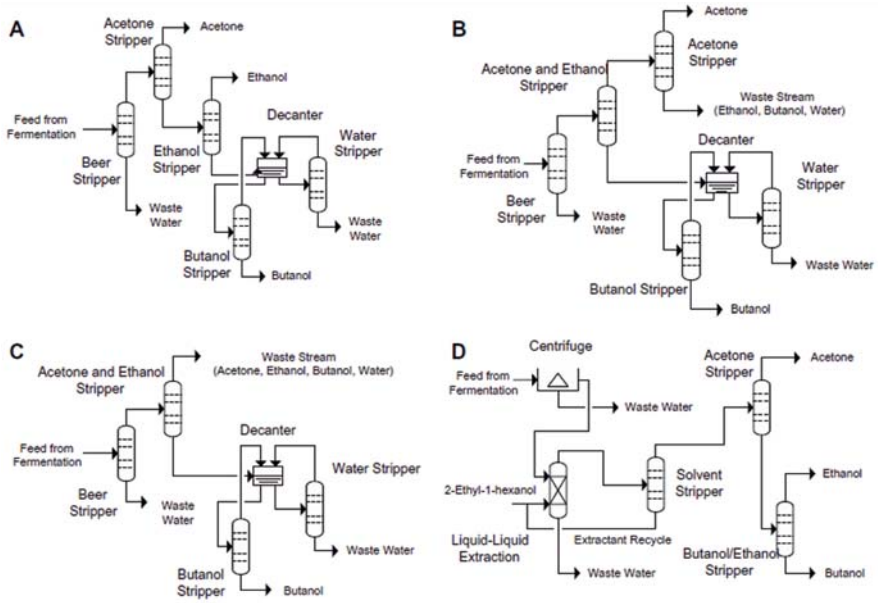

Figure 1. Flow diagrams for downstream processing of biobutanol (vd Merwe et al., 2012)

2. Problem statement

The production cost of the conventional acetone-butanol-ethanol (ABE) fermentation process using Clostridium spp. is higher than that of petro-processes, mainly due to the low butanol titer, yield, and productivity in bioprocesses. In particular, a low butanol titer leads to extremely high recovery costs. The conventional recovery by distillation is an energy-intensive process, which has largely restricted the economic production of biobutanol. Recent reviews include other butanol recovery process based on gas stripping, liquid-liquid extraction, adsorption, and membrane-based techniques. However, all these process require 5-7 operating units (leading to high capital cost) and an energy intensive operation due to the bulk removal of water from the diluted fermentation broth (about 2% because of the solvent toxicity to the micro-organism).

Figure 1 illustrates some of the options described in literature (vd Merwe et al., 2012). The problem is that all these designs have some major drawbacks that hinder their implementation in practice. In designs A, B and C, the ethanol column must achieve very high recovery of this component. Otherwise, because the butanol / water separation delivers the products as bottom streams of distillation columns, ethanol (the lightest component) will accumulate in the recycle streams. This has a negative impact not only on the investment and operating costs, but also on the process controllability. Design D incurs additional costs due to use of a large amount of solvent for water recovery.

To solve these problems, we propose a novel separation sequence able to reduce the costs of the down-stream distillation of butanol. The improvements include: 1) the column separating ethanol is part of the recycle loop of the butanol-water separation, in order to prevent ethanol accumulation; 2) the first unit of the sequence is a decanter, preventing phase separation in the first distillation columns. Rigorous dynamic simulations are also used to prove the controllability of the proposed process.

3. Modelling approach

The process was simulated in Aspen Plus using the NRTL property model that is most suitable for these components and conditions and in line with the recommendations for such systems (Kiss, 2013). All the binary interaction parameters related to the property model are available in the pure components databank of the Aspen Plus process simulator. Experimental data (Lee et al., 2004) was used to check that the butanol / water LLE is correctly predicted by the NRTL model with default Aspen Plus binary interaction parameters (Figure 2, left). Occurrence of a heterogeneous azeotrope (Figure 2, right) is a feature of the butanol – water mixture which is neatly exploited in order to cross the distillation boundary and therefore produce high purity products.

Jin et al. (2011) described several integrated systems for fermentation and in situ solvent recovery where the ABE fermentation process is coupled with gas stripping, liquid-liquid extraction (perstraction), and pervaporation. Among them, gas stripping is a quite simple technique for recovering ABE from the fermentation broth. Nitrogen or fermentation gases (CO_2 and H_2) are bubbled through the broth and capture the solvents (butanol or ABE). Then the gas is passed through a condenser. The liquid solvents are collected, while the gas is recycled back to fermenter to get more solvents. This allows the collection of a more concentrated ABE mixture (4.5 %wt acetone, 18.6 %wt butanol and 0.9 %wt ethanol) that is further treated by down-stream processing. The focus of this paper is on the efficient down-stream processing of the effluent stream from an ABE fermentation process coupled with gas stripping (Jin et al., 2011).

4. Results and discussion

In spite of being considered the most energy intensive separation, distillation remains a method of choice for the separation of fluid mixtures (Kiss, 2014). Figure 3 presents the flowsheet of a new down-stream processing sequence for the ABE process, including the control structure along with the mass balance and the key design parameters. The first unit of the sequence is a decanter that prevents potential phase separations in the distillation columns. The organic phase (rich in butanol) goes to first stripping column (COL-1) that separates butanol as bottom product and a water rich top stream which is recycled to the decanter. The aqueous phase from the decanter is fed to the stripping column (COL-2) that separates water as bottom product (main water outlet).

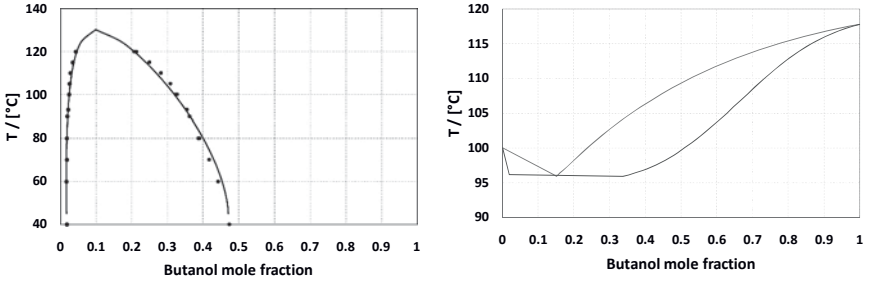

Figure 2. Phase equilibrium of mixture butanol-water. Left: Comparison between LLE predicted by NRTL model (line) and experimental data (dots; Lee et al., 2004); Right: T-xy diagram, showing the occurrence of a heterogeneous azeotrope (1 bar).

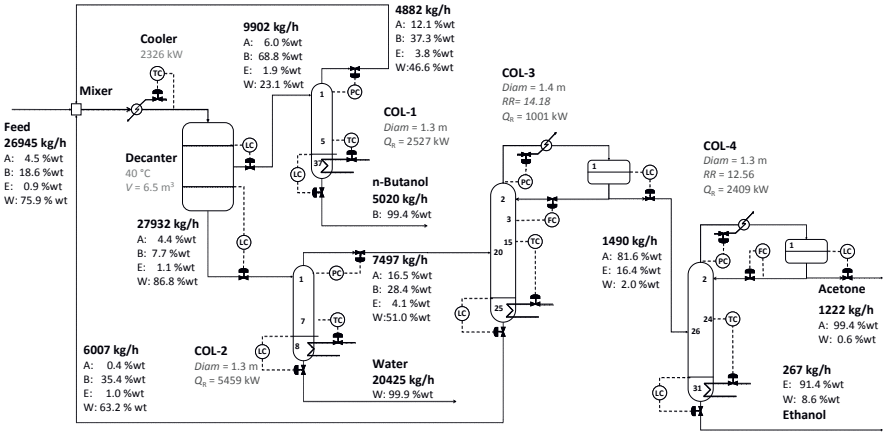

Figure 3. Process flowsheet of the novel down-stream separation sequence (40 ktpy butanol)

The top stream of the stripping column (COL-2) is fed to the distillation column (COL-3) that separates an acetone-ethanol rich fraction as top distillate stream and a butanol-water bottom stream that is recycled to the decanter. The acetone-ethanol stream from this column (COL-3) is sent to distillation column (COL-4) that separates near azeotropic ethanol as bottom product and acetone as top distillate. The column separating ethanol (COL-3), which is part of the recycle loop of the butanol-water separation, prevents ethanol accumulation although a high value for the ethanol recovery in the distillate is not required. Figure 4 shows the liquid composition profiles along the four columns. Due to high purity requirements, quite a large number of trays are necessary for the columns delivering the butanol, acetone and ethanol products (COL-1 and COL-4). However, the splits (water, butanol) / (water) and (acetone, ethanol) / (water, butanol) are rather easy and they can be achieved with a low number of trays (COL-2 and COL-3).

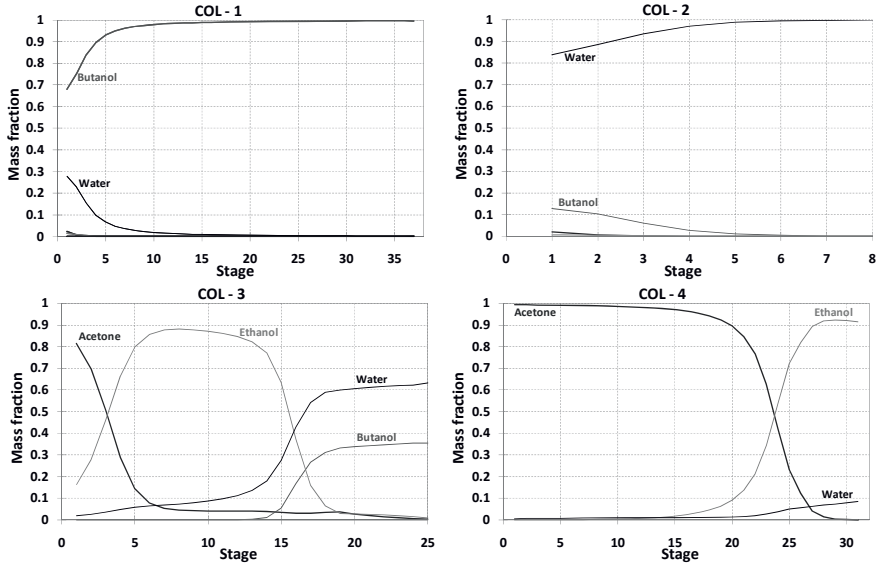

Figure 4. Molar composition profiles in the stripping and distillation columns

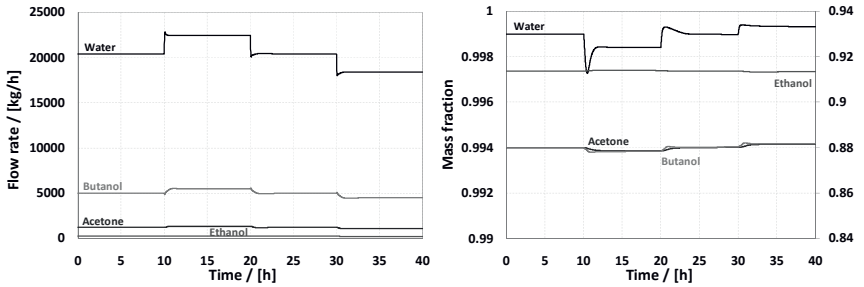

Figure 5. Dynamic simulations results: flow rates (left) and composition (right)

After developing the base case, the design was optimized using the total annual cost as objective function to be minimized: TAC = OpEx + CapEx / 3. The design parameters (e.g. number of trays, feed tray, reflux ratio) were used as decision variables. A payback period of 3 years and 8000 hours/year operating time was assumed. The capital cost was evaluated according to Dimian (2003). The heating and cooling costs taken into account are: LP steam (6 bar, 160 °C, $7.78/GJ), and cooling water ($0.72/GJ).

A dynamic simulation was built in Aspen Dynamics. All vessels were sized based on 15 minutes residence time. The control structure involves simple controllers, chosen as PI and tuned by the direct-synthesis method. The results of dynamic simulation are given in Figure 5. The simulation starts from steady state. At time t = 10 h, the feed flow rate is increased by 10%, then at time t = 20 h, the feed flow rate returns to its original value, and at time t = 30 h, the feed flow rate is reduced by 10%. Remarkable, all disturbances are properly rejected, with low overshooting and short response times.

5. Process evaluation

Table 1 lists the equipment cost, energy requirements and the total annual cost (TAC). The total equipment cost takes into account the decanter and all distillation columns (including heat exchangers: reboilers and condensers) and amounts 4420 k$, while the total operating costs (energy related) are 2681 k$/yr. The specific energy requirement is 2.28 kWh/kg butanol, which is in the same range as for the bioethanol production. However, in case of the ABE process, each kg of butanol yields also 0.243 kg acetone (high purity) and 0.054 kg ethanol (near azeotropic composition with water) by-products which are valuable and contribute positive to the economics.

Table 1. Economic evaluation of the enhanced ABE down-stream processing

Item description (unit)	**COL - 1**	**COL - 2**	**COL – 3**	**COL - 4**	**Decanter**
Shell / [10^3 US$]	292.7	107.49	250.31	267.9	71.22
Trays / [10^3 US$]	28.69	6.51	23.05	25.47	-
Condenser / [10^3 US$]	-	-	557.02	560.75	303.9
Reboiler / [10^3 US$]	567.05	788.19	245.62	325.33	-
Heating / [10^3 US$/year]	566.29	1223.24	224.47	539.81	-
Cooling / [10^3 US$/year]	-	-	77.06	50.18	11.52
TAC / [10^3 US$/year]	862.46	1523.98	660.21	983.16	136.56

6. Conclusions

The enhanced new down-stream processing sequence proposed in this work allows the efficient separation of butanol using fewer equipment units and less energy as compared to previously reported studies (vd Merwe et al., 2012; Errico et al., 2015). The main improvements include using a decanter as the first unit of the separation sequence to prevent phase separation in the stripping and distillation columns, and placing the column separating ethanol in the recycle loop of the butanol-water separation to prevent ethanol accumulation. The total equipment cost is 4420 k$, while the energy costs are 2681 k$/yr. The energy requirement for separation is very low (2.28 kWh/kg butanol), especially considering that butanol fuel has a specific energy of 10 kWh/kg (36 MJ/kg).

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