Isopropanol/ n -Butanol/ ethanol separation from diluted fermentation broth by distillation. Process optimization using Mixed Integer Linear Programming (MILP) techniques

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Abstract

This work has been performed in the framework of the development of the bio-based fermentation process to produce IBE (isopropanol/ n-butanol/ ethanol). The so-called IBE fermentation is indeed an interesting sustainable alternative to produce fossil-based products. However, product inhibition in fermentation leads to dilute fermentation broths in water (15-25 g IBE/L) which implies high energy demand for products/water separation. In the present study focus has been put on ready-to-industrialize downstream processes for Isopropanol/ n-Butanol/ Ethanol separation from dilute fermentation broth, using conventional distillation and shell-and-tube heat-exchanger technologies. A reference process scheme, using 5 distillation columns, as well as an IFPEN patented distillation sequence with 3 columns only were optimized using an in-house tool. The tool allows to simultaneously optimize the heat exchanger network configuration and the distillation columns' operating pressures for a given material balance, using Mixed Integer Linear Programming (MILP) optimization techniques. When comparing to the reference process, the optimized heat exchanger network leads to significant vapor consumption reduction and to also significant total separation cost reduction, when both investments and utilities costs are considered. The IFPEN patented scheme even without optimization is found to be more interesting than the reference scheme and is shown to be even more interesting after optimization. The tool can be applied to any distillation process, leading to significant cost savings.

Keywords: Isopropanol/ n-Butanol/ Ethanol fermentation, Distillation, Optimization, Mixed Integer Linear Programming

1. Introduction

N-butanol is used as a solvent and could be used as a fuel. It reached 4.1 million tons consumption in 2015. Isopropanol, a 1.9 million tons market in 2015, can also be used as a solvent and has also shown its interest as an additive in fuels. Finally, isopropanol can also be transformed into propylene, a major chemical intermediate today.

N-butanol and isopropanol are currently produced by petrochemical routes, but new technological routes are under development including bio-based technologies. Their production can be carried out by fermentation, e.g. ABE production (acetone, n-butanol, and ethanol) or IBE production (isopropanol, n-butanol, ethanol). The ABE process using *Clostridium*-type bacteria was one of the first large-scale industrial microbial process for chemical production, as well as the largest fermentation process under sterile conditions (Ni, 2009; Köpke, 2011). Initially, acetone was the main compound of interest for its use in the production of cordite during World War I and its use in the production of other chemicals. Nowadays, acetone is sometimes considered as an undesirable by-product due to its low properties as a biofuel or chemical. The reduction of acetone into isopropanol is possible using different bacteria belonging to the genus *Clostridium*. The production process of IBE is therefore based on the ABE fermentation process and uses strains of the genus *Clostridium* capable of fermenting simple sugars and reducing a large part of the acetone into isopropanol. However, a small part of acetone is still produced during IBE fermentations.

N-butanol production by *Clostridium*-type strains, for both ABE and IBE fermentations, is limited by its impact towards microbial growth, typically when its concentration is between 7 and 15 g/L. This greatly limits the final alcohol concentration of the fermentation broth, to approximately 10 to 30 IBE g/L. Let's note at this point that some aspects of ABE process can easily be used for IBE process: for example, n-butanol inhibition in fermentation leads to the same issues of diluted broth separation.

Such low concentrations imply high energy demand for products/water separation and therefore high separation costs. Several solutions have been reviewed in literature to achieve cost reduction (Kujawska, 2015; Vane, 2008). A part of them concerns the downstream process, i.e. alcohol/water and alcohol/alcohol separations. Hybrid distillation/liquid-liquid extraction processes using solvents have been proposed, mesitylene has been considered by Kraemer (2010, 2011) –, and ethylene glycol by Zhang (2020). Mesitylene appears to be an interesting solution as far as energy demand is concerned, but capital cost investment is not given. Moreover, after alcohol separation, the vinasses are meant to be recycled to the fermenter, and the residual mesitylene's toxicity to micro-organisms must be investigated. For ethylene glycol, the authors use n-butanol in higher concentration of about 4.46 wt %, which further implies low energy demand for separation but is hard to achieve with ABE/ IBE fermentation. Another way to achieve separation cost reduction is to increase alcohol concentration in broth. In order to limit n-butanol inhibition on bacteria, In Situ Product Recovery Techniques (ISPR), consisting in removing n-butanol from the fermenter during its production, have been considered (Outram, 2016). A part of these techniques, such as perstraction, are at research level and would need significant development before industrial level. Gas stripping (Xue, 2012) or two-phase fermentation (González-Peñas, 2020) in the presence of a biocompatible solvent in the fermenter are two types of techniques nearer to industrial scale. However, those techniques are relatively expensive and there is no evidence that the cost of ISPR techniques is offset by the decrease in separation costs as several parameters must be considered. It would then be important to properly estimate the cost/benefit ratio of ISPR techniques.

In the present study focus has been put on ready-to-industrialize downstream processes for isopropanol/ n-butanol/ ethanol separation from dilute fermentation broth, using conventional distillation and shell-and-tube heat-exchanger technologies. The originality of the work consists here in a thorough process study including both process flow scheme optimization and an associated techno-economic estimation.

2. Methods

As aforementioned, the IBE process is close to the ABE process. For the downstream separation part, the main difference is that, unlike acetone, isopropanol forms an azeotrope with water which makes infeasible the complete dehydration of isopropanol by conventional distillation: for example, at atmospheric pressure, the isopropanol-water azeotrope contains 12 wt % of water. . Moreover, that little amount (approx. 0.2 - 0.6 g/L) of acetone is still being produced, which represents an undesirable impurity to be eliminated from the main products.

2.1. Process description. 5 columns distillation process – reference case.
The reference distillation process was adapted from the ABE literature (van der Merwe, 2013) and is shown in Fig. 1. It involves five distillation columns to perform the separation of the various components. The Beer column recovers IBE at the top and eliminates 98.7 % of water at the bottom. The Acetone column allows the elimination of undesired acetone. With the IPA column, it is possible to separate the isopropanol/ water azeotrope and the small amount of ethanol at the top. The Water and Butanol columns are the last two columns used to break the water/n-butanol heterogenous azeotrope and recover the n-butanol at the bottom of the Butanol column.

2.2. Process description. 3 columns distillation process – base case
Another way to achieve the required separation is to use the sequence adapted from an IFPEN patent (Mikitenko, 1983) discussed by Pucci (1986) and shown in Fig. 2. This sequence consists only of a Beer column and a second column to separate the butanol from the other components. These are finally sent to a third column which separates isopropanol/water azeotrope and ethanol from the undesired acetone. The particularity of this scheme is in the second column. This column provides a three-phase area (two liquid and one vapor) on some trays. The aqueous phase is subtracted from the three-phase zone and is recycled and mixed with the feed of the first column.

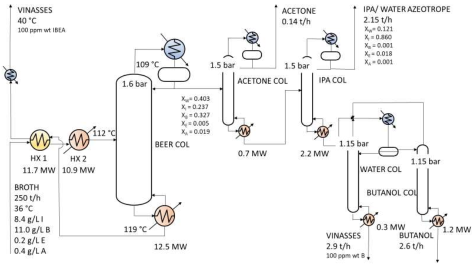

Fig 1. Flowsheet of the 5 columns reference case

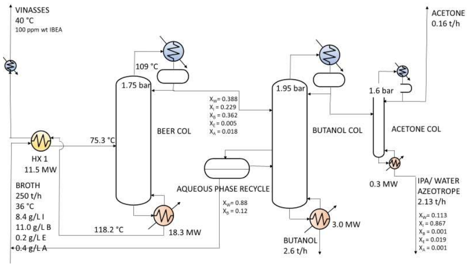

Fig 2. Flowsheet of the 3 columns base case

2.3. Flowsheet simulation
The flowsheets were simulated using SIMSCI's PRO/II v 10.2 software. The base thermodynamic method used was SRK-Simsci (SRKS). The unary and binary, both for vapor/liquid and liquid/liquid equilibria, were adjusted based on literature and in-house experimental data.

2.4. Process optimization using Mixed Integer Linear Programming (MILP) techniques
To achieve separation cost reduction, including both investments and utilities, the two process schemes were optimized with an in-house optimization tool, based on Mixed Integer Linear Programming (MILP) techniques. Fig 3. shows the general optimization procedure.
The global material balances, as shown in Fig. 1. and 2. are kept constant for the whole study. First, data are generated using PRO/II v 10.2 process simulation software. A linear equation set, including temperature vs. enthalpy curves for process streams at different pressures, energy consumption vs pressure with different number of trays for columns and utility consumption is coded into GAMS Studio V 25.1.2 after equation parameter fitting using Microsoft Excel. The novelties of the model stay in the fact that on the one hand streams can either give or receive heat, i.e. they are not mandatorily defined as hot

or cold streams, and on the other hand the column's operating pressures are simultaneously optimized with the heat exchanger network, i.e., the pressures of some of them are adapted in order to allow reboiler/condenser integration between columns. Some extra features, such as steam and electricity generation are also enabled by the model but not used in the current study. The goal is to maximize process/process energy integration, thus minimizing utility consumption while considering penalties for extra investment costs due extra heat exchangers or extra number of trays for columns. The objective function, calculated in €/h, is the sum of utilities consumption and production, and investment penalties. The objective function is then minimized using CPLEX 12.10 solver provided by GAMS Studio V 25.1.2. As a result, we get an optimized heat exchanger network and column's operating pressures and an idea of optimum number of trays. To end with, the resulting heat exchanger network is integrated in the flowsheet and used to determine real utility consumption, equipment are sized, and investment cost determined to end up with total separation cost, in €/t of IBE.

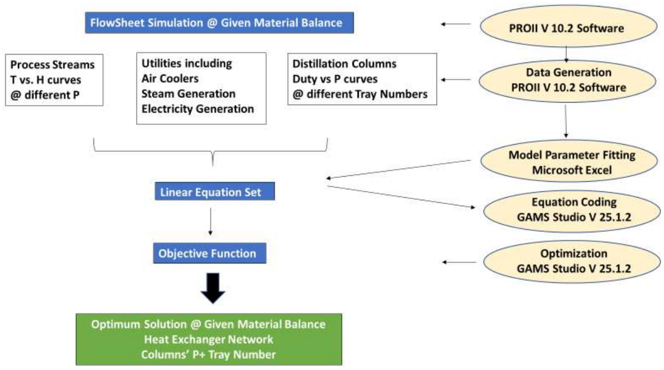

Fig 3. Optimization procedure

3. Results and discussion

3.1. Optimized 5 columns distillation process. Energy demand.

The resulting flowsheet is shown in Fig. 4. First, the optimized scheme shows an integration between the IPA and the Butanol columns. The operating pressure of the first is raised to 5.5 bars, thus rising temperature level of the condenser, and allowing its condensation heat recovery by the Butanol column's reboiler. Moreover, liquid-liquid demixtion is no longer present at this level of pressure in the IPA column, leading to cheaper column internals and easier operation.

The main part of the optimization concerns the pre-heating of the fermentation broth and the Beer column's reboiler duty. Indeed, heat can be recovered not only from the bottom effluent of the column (the so-called vinasses), but also from the top, requiring two extra exchangers. The broth is divided into two streams, one part recovering heat from the vinasses and the other from the top stream. After remixing of the two streams, extra 1.9 MW can be indeed recovered from the top. In the reference case 10.9 MW (HX 2- pre-heater, see Fig.1.) + 12.5 MW (Beer column reboiler), so 23.4 MW of low-pressure steam was necessary to achieve the required separation, while in the optimized case 13.9 MW are sufficient. The operating pressure of the Beer column was slightly increased compared to the reference case to compensate extra pressure drop from the extra heat exchangers.

3.2. Optimized 3 columns distillation process. Energy demand.

The resulting flowsheet is shown in Fig. 5. The main idea is roughly the same than for the 5 columns process. Extra heat can be recovered from the top of the Beer Column. The vinasses transfer heat to the broth in two heat exchangers (HX 6 and HX 1) and recover heat from the top in heat-exchanger HX7. Low-pressure steam consumption falls from 18.3 MW to 15.4 MW, requiring two extra heat exchangers.

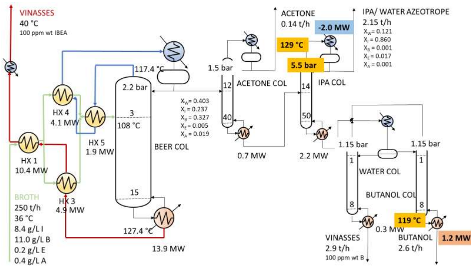

Fig 4. Optimized 5 columns flowsheet

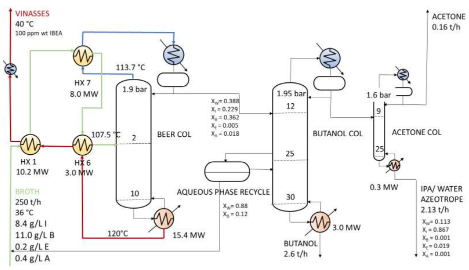

Fig 5. Optimized 3 columns flowsheet

3.3. Total separation cost

For both distillation sequences, hot utility demand remarkably decreases when optimized. The total separation cost, including total utilities consumption and investment costs has further been calculated. The results, given in normalized to 100 base are shown in Fig 6. The 3 columns optimized process ends up being 34% cheaper than the reference case. Because of the liquid-liquid demixtion zone in the Butanol column of this process, it may however be hard to operate. In that view, the more classical, optimized 5 columns process, with 28 % lower separation cost compared to the reference case can be considered as the best solution.

3.4. Alternative solutions

Vapor recompression of the Beer column's top stream to provide heat to the bottom could be an option, considering the 10 °C temperature difference between the top and bottom tray temperatures. Nevertheless, after total separation cost calculation, even if this solution is interesting from utility consumption point of view, the investment cost of the compressor appears to be too high, as it is shown in Fig. 6.

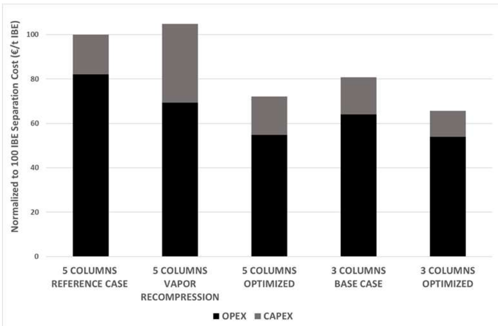

Fig 6. Optimization results @ 20 g/L IBE in broth

To end with, aforementioned ISPR processes could lead to broth concentrations above 25 g IBE /L. Fig 7. shows that the relative gain on separation tends to decrease in this concentration region.

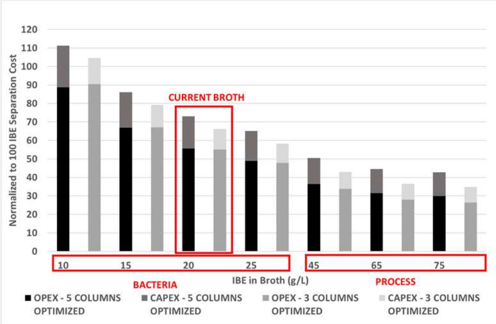

Fig 7. Influence of broth concentration on separation cost

4. Conclusions

The IFPEN process optimization tool allowed to identify process flow scheme with heat exchanger integration with significant decrease in the IBE fermentation downstream process cost. It is shown here that up to 30% reduction in production cost can be achieved. This tool can be applied to any distillation process to lead to economically interesting distillation processes which is especially of great importance for bio-based processes.

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