Simulation and energy analysis of the ABE fermentation integrated with gas stripping

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Abstract

Acetone-Butanol-Ethanol (ABE) fermentation has recently gained renewed attention in the context of biorefinery approaches for the production of fuels and chemicals from renewable resources.

The main problem associated with the ABE fermentation by microorganisms is the self-inhibition of the process due to butanol toxicity to the culture, which limits the application on an industrial scale. The use of a separation method, which enables selective removal of toxic components from the fermentation broth, may contribute to improve the economics of such process. In this context, different recovery techniques have been investigated, including gas stripping. Several literature experimental studies on lab-scale integrated gas stripping units are available, but few deal with process simulation.

This work concerns the recovery of butanol from a batch fermenter, in which the ABE mixture is recovered from the broth by means of gas stripping and, subsequently, fractionated in a distillation train. The aim of this work is to compare the performances of the integrated fermentation-gas stripping process with those of a conventional batch fermenter. For this purpose, both processes have been modeled and their energy requirements have been determined by means of an energy analysis. Results show that product removal has a beneficial effect on sugar consumption and process productivity at the expense of an increased energy demand.

Keywords: bio-butanol, ABE fermentation, integrated product recovery, gas stripping, inhibitors removal, process intensification.

1. Introduction

The increasing greenhouse gas emissions and the resulting global climate change, joined with a growing world population, are key challenges that are leading to an increased interest in processes able to produce fuels and chemicals from alternative, renewable resources.

Butanol is an important commodity chemical and an attractive biofuel, which shows several
advantages over ethanol [1]. It can be produced through the Acetone-Butanol-Ethanol (ABE) fermentation by clostridia. However, the fermentation is limited by product inhibition, especially due to butanol, and only 22 g/L of total solvents with a butanol concentration lower than 13 g/L are typically obtained in the bioreactor during a batch process [2].

Therefore, the ABE fermentation is characterized by high process costs, due to the large volumes required and the downstream product recovery from dilute broths, usually performed by distillation. The application of integrated recovery techniques that remove butanol from the broth during fermentation represents a viable solution to solve the problems related to the ABE fermentation and to increase the profitability of the process [3]. In fact, product recovery reduces the effects of product inhibition and allows increasing the process productivity. The operating costs for product recovery are expected to decrease for higher concentrations of ABE in the mixture to be treated.

In an integrated process, products can be separated from the fermentation broth either within the reactor or by circulating the broth through an external separation unit. These two techniques are referred to as in-situ and ex-situ, respectively [4].

The most mature product removal techniques include gas stripping, solvent extraction, adsorption, vacuum fermentation, pervaporation and perstraction [5].

Gas stripping shows several advantages over other techniques. It is simple to operate and scale-up, it does not require expensive equipment, it does not remove nutrients and intermediates from the broth and it is not harmful to the fermentation microorganism [6]. Several literature works reported the effect of butanol titer in the broth on the stripping process. In this respect, Xue et al. [7] reported that it is necessary to conduct gas stripping at a butanol concentration higher than 8 g/L in the feed solution in order to obtain a condensate with a butanol titer higher than its solubility in water, which results in phase separation.

The effects of application of in-situ gas stripping on the ABE fermentation have been widely studied, demonstrating the reduction of product toxicity and the resulting improvements in productivity [8].

However, only a few papers appeared dealing with the energy demand associated with this technique. Oudshoorn et al. [9] reported an energy demand in the range of 14-31 MJ/kg of produced butanol considering a steady-state process for the separation of a water-butanol binary mixture. Groot et al. [10] considered a two-column system, neglecting the complete separation of acetone and ethanol, obtaining an energy requirement of 21 MJ/kg_{ABE}. Outram et al. [11] compared different in-situ product recovery techniques for the separation of acetone, butanol and ethanol from a batch reactor. However, they adopted a simplified representation of the fermenter that was modeled as a stoichiometric, continuous, steady-state reactor. The continuous stream from the fermenter was
assumed to represent the desired conditions in the reactor and the fermentation broth was not recycled to the fermenter after the in-situ recovery had been applied.

In this work, the effect of the integrated recovery by gas stripping on the whole ABE production process has been studied.

Dynamic simulations of the batch fermentation have been performed in order to investigate the beneficial effect of product removal on the process productivity and to compute the actual concentration levels of the stream sent to the stripping column. Process simulations have allowed to assess the effectiveness of the integrated product recovery technique and the overall energy demand. The integrated process has been finally compared with a traditional batch fermentation, both followed by downstream fractionation of the solvents, in order to investigate the potential advantages of the process intensification.

2. Thermodynamic Framework

Thermodynamics plays an important role in process simulation, allowing to properly describe the phase equilibrium conditions involved in the process under study. The ABE mixture contains many polar compounds and, thus, shows a strong non-ideal behavior, with components pairs also forming azeotropic systems. In addition to this, butanol and water exhibit a miscibility gap, whose correct representation is fundamental for the proper description of the separation process. Therefore, the thermodynamic model must be able to properly describe both Vapor-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) conditions.

Considering the non-ideal behavior of the system under study, an indirect $\gamma/\phi$ method (NRTL-RK) has been chosen in this work for its thermodynamic characterization. It is based on the Non-Random Two-Liquid (NRTL) model [12] and on the Redlich-Kwong (RK) Equation of State (EoS) [13] for the calculation, respectively, of the activity coefficient in the liquid phase and of the fugacity coefficient in the vapor phase. The considered components have been only those effectively removed from the broth, namely acetone, butanol, ethanol, water, and the stripping agent, nitrogen. Firstly, the capability of the model to reproduce phase equilibria using default parameters implemented in the Aspen Plus® process simulator has been checked. Then, the model parameters have been regressed to improve model predictions, making use of many binary and ternary VLE and LLE data available in the literature [14]. Nitrogen has been treated as a Henry component and its Henry’s law constants have been kept equal to default values. The regressed parameters (reported in Table 1, where acetone, butanol, ethanol and water are denoted by A, B, E and W, respectively) have been implemented in Aspen Plus® [15], chosen for the simulation of the distillation process aimed at recovering acetone, ethanol and butanol downstream of the fermentation process. Those concerning the ethanol-butanol
and the ethanol-water pairs are not reported in Table 1 because the parameters available in the simulator have been used for them, being already suitable for satisfactorily reproducing the experimental data.

Table 1. Regressed parameters for the NRTL-RK thermodynamic model.

<table>
<thead>
<tr>
<th>i</th>
<th>A</th>
<th>A</th>
<th>B</th>
<th>E</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>j</td>
<td>W</td>
<td>B</td>
<td>E</td>
<td>W</td>
<td></td>
</tr>
<tr>
<td>a_{ij}</td>
<td>-1.6803</td>
<td>3.9225</td>
<td>-2.2512</td>
<td>-2.0447</td>
<td></td>
</tr>
<tr>
<td>a_{ji}</td>
<td>4.9929</td>
<td>-3.2661</td>
<td>2.3301</td>
<td>4.2834</td>
<td></td>
</tr>
<tr>
<td>b_{ij}</td>
<td>860.74</td>
<td>-1273.33</td>
<td>879.45</td>
<td>980.98</td>
<td></td>
</tr>
<tr>
<td>b_{ji}</td>
<td>-1078.63</td>
<td>1196.83</td>
<td>-666.71</td>
<td>-239.15</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>0.5149</td>
<td>0.3000</td>
<td>0.8006</td>
<td>0.4454</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 represents the temperature-composition diagram for the system water-butanol at 1 atm. The comparison with the experimental data [16-23] shows a better agreement with the predictions by the proposed model rather than with those by the default model, especially in the LLE region.

The model has been also applied to the ternary systems acetone-water-butanol and ethanol-water-butanol and validated by comparison with the experimental data available in the literature. Results are illustrated in the ternary diagrams shown in Fig. 2 for the system with acetone and in Fig. 3 for the system with ethanol.

3. Process Description

In this work, the classical batch fermentation process has been compared with an alternative process solution, which involves a gas stripping operation aimed at removing the fermentation products from the broth in order to reduce inhibition. As reported in the literature, either nitrogen or the fermentation gases (i.e., CO₂ and H₂) can be used for this purpose. However, the use of CO₂ can alter the pH of the fermentation broth, which is a parameter of paramount importance for the stability of the fermentation. Therefore, nitrogen has been considered as stripping agent and an ex-situ removal of the fermentation products has been preferred to an in-situ one, in order to reach higher performances in a multi-stage rather than in a single-stage unit and without disturbing the fermentation.
Fig. 4 shows the scheme of the integrated process. The fermentation broth is withdrawn from the fermenter and fed to the stripping column at a time when the microorganism starts to be inhibited by the solvents. The fermentation broth depleted from the components stripped by nitrogen is then recycled back to the fermenter. As for the vapor stream leaving the stripping column, it is sent to a condenser, where it is cooled down to 3°C so that the stripped compounds are condensed and separated from nitrogen, which is recycled back to the stripping column after being heated-up to the fermentation temperature. A nitrogen make-up stream has been also considered to replace the losses occurring in the condensed stream. The composition of this stream is such that a phase separation occurs between a butanol-rich liquid phase (named ‘Organic phase’ in Fig. 4) and a water-rich liquid phase (named ‘Aqueous phase’ in Fig. 4).

The two liquid phases leaving the integrated fermenter-stripping process are collected in storage tanks and then sent to the distillation train for products fractionation, which is operated in continuous mode. The selected process scheme is the one described by Mariano et al. [26] and illustrated in Fig. 5.

The aqueous phase collected in the storage tank is mixed with the fermentation broth remained in the reactor. The resulting stream (named ‘FEED’ in Fig. 5) is fed to the beer column, after being pumped to 1.5 atm (i.e., the operating pressure of the beer column) and pre-heated to 93.4 °C by the bottom product obtained from this column, which separates the solvents (ABE) from the beer. The solvents, which are recovered at the top of the column, are cooled down providing heat to the reboiler of the downstream acetone column and ethanol column (described in the following) and further cooled down to 70°C before being expanded to 0.7 atm and mixed with the organic phase (named ‘ORGANIC’ in Fig. 5) leaving the integrated fermenter-stripping process. This stream is heated up from 3°C to 70°C and expanded to 0.7 atm before mixing with the ABE stream. The resulting mixture is treated in the four-column system also described by Mariano and coworkers [26]. In this system, the distillation columns are operated at different pressures in order to allow heat integration.

Acetone is separated in the acetone column, operated at 0.7 atm. As previously stated, the reboiler duty is met by condensing part of the overhead vapors from the beer column. The top product that meets commercial specifications is later compressed to atmospheric pressure and condensed.

The bottom product from the acetone column is cooled down to 50°C, expanded to 0.3 atm and further treated in the downstream ethanol column, which is operated at this pressure (vacuum operation allows the total reboiler duty to be met by condensing a part of the overhead vapors from the beer column).
A two-column distillation system in conjunction with a decanter is used to separate the heterogeneous binary butanol/water azeotrope. Thus, after being pumped to atmospheric pressure (i.e., the operating pressure of the water and butanol columns and of the decanter), the bottom stream of the ethanol column, is added to a decanter together with the top streams from the water and butanol columns. In the decanter, the butanol-rich liquid phase separates from the aqueous phase, forming an upper layer. The water-rich liquid phase is refluxed to the water column, whose bottom product contains almost pure water. On the other side, the butanol-rich liquid phase leaving the decanter is refluxed to the butanol column, which produces a high purity butanol product. The overhead vapors from the water and butanol columns are cooled down to 80°C, before they are sent back to the decanter.

The same scheme has been also used for the recovery of the solvents from the fermenter when it is not integrated with the gas stripping unit. The only difference lies in the composition of the stream fed to the beer column (which is the one of the broth remained in the fermenter when the reaction is stopped) and in the absence of the organic stream, which is mixed with the overhead vapors of the beer column and sent to the acetone column in the scheme shown in Fig. 5.

4. Modeling

The process studied in this work consists of two parts: the integrated fermenter, operated in batch mode, and the distillation train for product fractionation, operated continuously.

Since the integrated recovery process is a non-conventional unit, it has been modeled by means of an in-house Fortran routine. On the contrary, the downstream separation process consists of conventional unit operations and, thus, it has been simulated using a commercially available simulation software (Aspen Plus® [15]).

The kinetic model used for simulating the reactor is the one proposed by Mulchandani and Volesky [27], which also accounts for the inhibition due to butanol and butyric acid (subscript ‘ba’) through the following function $f$:

$$f = \exp\left(-0.01 \cdot (C_B + C_{ba})\right) \quad \text{for} \quad (C_B + C_{ba}) \leq 8 \text{ g/L} \quad (1)$$

$$f = 2.16 - 0.153 \cdot (C_B + C_{ba}) \quad \text{for} \quad 8 \leq (C_B + C_{ba}) \leq 13.9 \text{ g/L} \quad (2)$$

The reactor model equations are of the form given by Eq. (3), in which $r_i$ and $C_i$ denote, respectively, the rate of reaction and the concentration of the $i$-th component inside the reactor (i.e., the microorganism, substrate, butyric acid, acetic acid, butanol, acetone, ethanol and water). To model the integrated scheme shown in Fig. 4, the material balance equations have been modified with respect
to the ones for a classical batch fermenter to account for the integration between the fermenter and
the stripping unit by using two parameters: the removal function, $\eta_i$, and the dilution factor, $D_f$.

\[
\frac{dC_i}{dt} = r_i - \eta_i \cdot D_f \cdot C_i
\]  

(3)

The dilution factor corresponds to the ratio between the volumetric flow rate withdrawn from the
reactor and the reactor volume. If the dilution factor is zero, Eq. (3) reduces to the one that
characterizes the behavior of a classic batch reactor.

Only the volatile components (namely, acetone, butanol, ethanol and water) have been considered
to be removed by gas stripping (as reported in the literature by Ezeji et al. [6]), assuming the removal
to be instantaneous and the reaction volume to remain constant. For each of these components, a
removal function defined as the ratio between its molar flow rate in the condensed phase and that in
the broth entering the stripping column has been considered. The removal functions have been
obtained by regression of the results obtained from simulations performed in Aspen Hysys® [28] for
different broth compositions in terms of solvents concentrations, which have been varied in the range
of values typically observed in the fermenter. In these simulations, an atmospheric stripping column
with 10 theoretical stages has been used and the liquid and gas phases enter it at 32°C. Moreover, the
liquid-to-gas ratio has been set to 2 (on a molar basis): this value allows to maximize the recovery of
solvents from the fermentation broth [29].

Eq. (3) has been written for each considered component and the resulting ordinary differential
equation system has been solved in Fortran using the DLSODES solver from ODEPACK [30].

At the end of the fermentation, the mass of each component, $m_{F,i}$, remaining in the fermentation
broth inside the reactor is computed as:

\[
m_{F,i} = C_i(t_F) \cdot V_F
\]  

(4)

in which $C_i(t_F)$ represents the concentration of component $i$ in the fermentation broth at the end of the
fermentation and $V_F$ is the fermenter volume.

In the integrated process, the mass flowrates, $\dot{m}_{S,i}$, of the components removed from the reactor by
the stripping column and collected in the condensate are computed as:

\[
\dot{m}_{S,i} = \eta_i \cdot D_f \cdot c_i \cdot V_F
\]  

(5)
The solvents stripped during the process are condensed and the obtained organic and aqueous phases are, then, collected in storage tanks. The final mass of each component in the storage tanks is computed integrating its mass flowrate over the fermentation time:

\[ m_{s,i} = \int_0^t \dot{m}_{s,i} \, dt \]  

As previously stated, the downstream ABE separation process has been simulated in the Aspen Plus® environment.

For the beer column, which consists of 50 theoretical plates and acts as a reboiled stripper, a mass recovery of 99.9% for the three components acetone, butanol and ethanol in the overhead vapor stream has been specified.

For the acetone column, the acetone mass purity (99.5 wt%) and the recovery (99.5%) have been specified, in addition to the number of stages (equal to 30).

The ethanol column has 50 stages, with the feed stream entering it at stage 14. In addition to the number of stages, the ethanol mass purity (85 wt%) and the recovery (95%) have been specified for the overhead product.

Finally, the water and butanol columns for the separation of the heterogeneous azeotrope consist of 10 stages, with feed at stage 1. Purities of 99.8 wt% for both the bottom products, namely water and butanol, have been specified.

### 5. Energy Analysis

To compare the performances of the two processes, the equivalent fuel approach has been applied. It has been already used in previous works [31, 32] in terms of equivalent methane in order to determine the amount of methane equivalent to a certain duty or work that must be supplied to or can be recovered from each equipment involved in the process. Similarly, in this work the amount of equivalent butanol has been determined as explained in the following, making use of its lower heating value (LHV) and of the cycle efficiencies (Table 2 summarizes the values used for each parameter in this work).
Table 2. Parameters used for the calculation of the equivalent amount of butanol consumed by the process.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV [MJ/kg]</td>
<td>33.11</td>
</tr>
<tr>
<td>$\eta_{CC}$</td>
<td>0.55</td>
</tr>
<tr>
<td>$\eta_{boiler}$</td>
<td>0.8</td>
</tr>
<tr>
<td>$\eta_{II}$</td>
<td>0.6</td>
</tr>
</tbody>
</table>

A certain amount of butanol must be consumed for producing low-pressure (LP) steam that provides heat to the reboilers of the beer column, of the water column and of the butanol column and to the organic fraction coming from the stripping unit. To account for this, LP steam has been considered to be generated by a butanol-fired boiler. The amount of equivalent butanol can be computed according to Eq. (7), given the boiler efficiency ($\eta_{boiler}$), the fuel lower heating value and the thermal duty to be provided to the process ($\dot{Q}$).

$$m_{FUEL} = \frac{\dot{Q}}{\eta_{boiler} \cdot LHV} \quad (7)$$

Condensation of the solvents contained in the vapor stream leaving the stripping column in the integrated process configuration shown in Fig. 4 (by cooling it down to 3°C) has been assumed to be achieved by a proper refrigeration cycle requiring electric power ($\dot{W}_{el}$) considered to be provided by a combined cycle. To calculate the amount of butanol equivalent to the required electric power, the coefficient of performance of the refrigeration cycle ($COP_R$) can be calculated from Eq. (8), where $\eta_{II}$ denotes the second principle efficiency and $COP_{R,id}$ stands for the coefficient of performance of an ideal Carnot cycle. It is given by Eq. (9) as a function of the temperatures of the hot and cold reservoirs ($T_{hot}$ and $T_{cold}$), assumed to be 30°C and -2°C, respectively, considering a minimum approach temperature of 5°C.

$$COP_R = COP_{R,id} \cdot \eta_{II} \quad (8)$$

$$COP_{R,id} = \frac{1}{\frac{T_{hot}}{T_{cold}} - 1} \quad (9)$$

By definition of the $COP_R$, the electric power can be computed given the cooling duty to be removed from the system (Eq. (10)).
\[ \dot{W}_{el} = \frac{\dot{Q}}{COP_R} \]  

Then, considering the definition of the efficiency of a combined cycle (\(\eta_{CC}\)) (Eq. (11)), which is given by the ratio between the electric power produced by the gas turbine and the steam turbine and the heat received by the gas turbine (given by the product of the fuel flow rate and its LHV), the amount of equivalent butanol can be determined according to Eq. (12).

\[ \eta_{CC} = \frac{\dot{W}_{el}}{\dot{m}_{FUEL} \cdot LHV} \]  

\[ \dot{m}_{FUEL} = \frac{\dot{Q}}{COP_R \cdot \eta_{CC} \cdot LHV} \]  

The electric energy to be provided to pumps and compressors has been assumed to be obtained by means of an equivalent butanol-fired combined cycle power plant. The amount of butanol equivalent to the required electric energy (\(\dot{W}_{el}\)) can be determined knowing the efficiency of the combined cycle and the fuel lower heating value (Eq. (13)).

\[ \dot{m}_{FUEL} = \frac{\dot{W}_{el}}{\eta_{CC} \cdot LHV} \]  

6. Results

6.1. Removal Functions

The removal functions used in the simulation of the integrated recovery process with gas stripping have been derived for acetone, butanol, ethanol and water based on the results obtained in Aspen Hysys® [28], as previously stated. The process scheme used in the simulation is the one reported in Fig. 4, where the concentrations of the solvents in the stream fed to the stripping column have been varied in such a way to cover all the concentrations experienced in the reactor during fermentation.

For each solvent, the removal function has been described with a linear dependence on its concentration, with the coefficients expressed as a function of the concentration levels of other solvents present in the broth. For water, the removal function has been computed from the water-butanol selectivity, in turn expressed as a linear function of butanol concentration in the broth.

The expression of the removal functions, of their coefficients and the corresponding coefficient of determination, \(R^2\), obtained by comparison with the simulation results are reported in Table 3.
Table 3. Removal functions for acetone, butanol, ethanol and water used in the modeling of the integrated fermenter-gas stripping process shown in Fig. 4.

### Acetone ($R^2 = 0.97$)

<table>
<thead>
<tr>
<th>Removal function</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_A = \eta_A(c_A) \cdot c_A + q_A(c_B)$</td>
<td>$a_1 = 4.615 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$m_A = a_1 \cdot c_A + a_2$</td>
<td>$a_2 = 5.990 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$q_A = a_3 \cdot c_A^3 + a_4 \cdot c_B + a_5$</td>
<td>$a_3 = -5.191 \cdot 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$a_4 = 3.665 \cdot 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$a_5 = 6.299 \cdot 10^{-2}$</td>
</tr>
</tbody>
</table>

### Butanol ($R^2 = 0.99$)

<table>
<thead>
<tr>
<th>Removal function</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_B = \eta_B(c_A) \cdot c_B + q_B(c_A)$</td>
<td>$b_1 = -1.954 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$m_B = b_1 \cdot c_A + b_2$</td>
<td>$b_2 = 7.456 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$q_B = b_3 \cdot c_A^3 + b_4 \cdot c_B + b_5$</td>
<td>$b_3 = 0$</td>
</tr>
<tr>
<td></td>
<td>$b_4 = 2.086 \cdot 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$b_5 = 1.112 \cdot 10^{-1}$</td>
</tr>
</tbody>
</table>

### Ethanol ($R^2 > 0.99$)

<table>
<thead>
<tr>
<th>Removal function</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_E = \eta_E(c_A) \cdot c_E + q_E(c_B)$</td>
<td>$e_1 = 1.146 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>$m_E = e_1 \cdot c_B + e_2$</td>
<td>$e_2 = 2.188 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$q_E = e_3 \cdot c_B^2 + e_4 \cdot c_B + e_5$</td>
<td>$e_3 = -4.994 \cdot 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$e_4 = 2.570 \cdot 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$e_5 = 8.187 \cdot 10^{-2}$</td>
</tr>
</tbody>
</table>

### Water ($R^2 = 0.99$)

<table>
<thead>
<tr>
<th>Removal function</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{WB} = \frac{\eta_W}{\eta_B} = m_{WB}(c_A) \cdot c_B + q_{WB}(c_A)$</td>
<td>$wb_1 = 1.292 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>$m_{WB} = wb_1 \cdot c_A + wb_2$</td>
<td>$wb_2 = -4.392 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$q_{WB} = wb_3 \cdot c_A^2 + wb_4 \cdot c_B + wb_5$</td>
<td>$wb_3 = 0$</td>
</tr>
<tr>
<td></td>
<td>$wb_4 = 2.570 \cdot 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$wb_5 = 8.187 \cdot 10^{-2}$</td>
</tr>
</tbody>
</table>

### 6.2. Process comparison

In this section, the results obtained from the simulations of the two processes (namely, the traditional batch fermentation process and the one integrated with gas stripping for solvents recovery, both followed by solvents separation by a five-column distillation train) are discussed for comparison purposes.

The concentration profiles inside the reactor obtained for the batch fermentation process are reported in Fig. 6. After 15 minutes, the concentrations of butanol and butyric acid reach the critical level for the inhibition of the fermentation microorganism, causing the interruption of the cell growth. At the same time, a reduction in the sugar consumption rate can be observed. The fermentation is ceased after 50 hours, when the butanol concentration is 20 g/L (37 g/L total ABE) and the sugar...
concentration is 10 g/L, corresponding to a substrate conversion equal to 88%. This situation is representative of a typical batch fermentation, in which the culture is unable to utilize all sugars due to the toxic effect of butanol.

For this case, the composition of the broth at the end of the fermentation is reported in Table 4. This stream is sent to the beer column of the distillation train for the recovery of the produced solvents. In the simulation of the train, only the desired solvents and water have been considered: the actual composition of the broth used in the simulations is reported in Table 5.

**Table 4.** Broth composition at the end of the batch fermentation process.

<table>
<thead>
<tr>
<th>Component</th>
<th>g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>3.05</td>
</tr>
<tr>
<td>Sugar</td>
<td>10.00</td>
</tr>
<tr>
<td>Butyric acid</td>
<td>1.17</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.11</td>
</tr>
<tr>
<td>Acetone</td>
<td>16.04</td>
</tr>
<tr>
<td>Butanol</td>
<td>20.11</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.11</td>
</tr>
</tbody>
</table>

**Table 5.** Composition (mole fraction) of the broth at the end of the batch fermentation process sent to the distillation train.

<table>
<thead>
<tr>
<th>Component</th>
<th>x_i</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>4.946·10^{-5}</td>
</tr>
<tr>
<td>Butanol</td>
<td>4.858·10^{-3}</td>
</tr>
<tr>
<td>Ethanol</td>
<td>4.333·10^{-4}</td>
</tr>
<tr>
<td>Water</td>
<td>0.9898</td>
</tr>
</tbody>
</table>

In order to reduce the toxic effect of butanol on cells, an integrated process of fermentation with gas stripping has been designed and simulated as described in Section 4. For this system, butanol and the other solvents are produced by the microorganism and removed through the stripping unit. The rate of butanol removal can be raised by increasing the dilution factor (i.e., the flowrate of the broth withdrawn from the reactor and sent to the stripping column), causing a reduction of the butanol concentration in the bioreactor. This would give a dilute butanol condensate, without obtaining the desired phase separation. Therefore, the dilution factor has been selected in such a way to obtain a butanol concentration in the fermenter lower than its toxic level, but high enough to obtain a
sufficiently concentrated butanol condensate. The selected dilution ratio of 0.32 h\(^{-1}\) allows to keep a constant butanol concentration of 10 g/L in the reactor during the whole fermentation.

The results obtained for this configuration, in terms of concentration profiles in the fermenter, are reported in Fig. 7.

The gas stripping process begins after 12 h, when the butanol concentration reaches 10 g/L, in order to avoid the inhibitory effect. The butanol concentration remains almost constant due to the continuous removal by the stripping column. A sugar conversion of 100% is obtained in 25 h, therefore reducing by 50% the fermentation time.

Fig. 8 shows the mass flowrates of the solvents removed through the stripping column during the fermentation, calculated according to Eq. (5).

The solvents stripped during the process are condensed and the obtained organic and aqueous phases are, then, collected in storage tanks. The final global composition of the condensate is reported in Table 6.

<table>
<thead>
<tr>
<th>Component</th>
<th>Global</th>
<th>Aqueous phase</th>
<th>Organic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>6.50·10(^{-3})</td>
<td>6.50·10(^{-3})</td>
<td>2.02·10(^{-2})</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.75·10(^{-2})</td>
<td>2.75·10(^{-2})</td>
<td>4.12·10(^{-1})</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.90·10(^{-3})</td>
<td>1.90·10(^{-3})</td>
<td>6.07·10(^{-3})</td>
</tr>
<tr>
<td>Water</td>
<td>0.9641</td>
<td>0.9641</td>
<td>0.5614</td>
</tr>
</tbody>
</table>

The total recovery of butanol in the condensate is equal to 44%, the rest remaining in the fermentation broth inside the reactor.

The butanol concentration in the condensate is high enough to obtain the phase separation, generating an organic phase consisting of 644.4 g/L of butanol, 24.7 g/L of acetone and 5.9 g/L of ethanol and an aqueous phase consisting of 101.5 g/L of butanol, 18.8 g/L of acetone and 4.4 g/L of ethanol.

However, it is worth highlighting that the organic phase contains only 0.1% of the recovered butanol, since the organic phase fraction after phase separation is only equal to 8.8·10\(^{-5}\). Therefore, most of the butanol has still to be recovered from the aqueous phase and both these streams are further treated in the downstream distillation train. For downstream processing, the aqueous phase of the
condensate is mixed with the fermentation broth remained in the reactor, giving the final composition reported in Table 7, and then fed together to the beer column. The organic phase, due to its high solvent content, is fed directly to the acetone column, bypassing the beer column.

Table 7. Composition (mole fraction) of the fermentation broth remaining in the reactor at the end of the integrated fermenter-gas stripping process and of the final aqueous phase obtained by mixing it with the aqueous phase of the condensate obtained downstream of gas stripping.

<table>
<thead>
<tr>
<th>Component</th>
<th>Fermentation broth</th>
<th>Final aqueous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>$2.54 \cdot 10^{-3}$</td>
<td>$2.84 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>Butanol</td>
<td>$2.38 \cdot 10^{-3}$</td>
<td>$4.29 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>Ethanol</td>
<td>$3.61 \cdot 10^{-4}$</td>
<td>$4.78 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Water</td>
<td>0.9947</td>
<td>0.9924</td>
</tr>
</tbody>
</table>

The results for the two studied configurations in terms of energy requirements are reported in Table 8.

Table 8. Comparison of process performances in terms of process productivity and energy consumption between the traditional batch fermentation process and the integrated fermenter-gas stripping process.

<table>
<thead>
<tr>
<th></th>
<th>Batch fermentation</th>
<th>Integrated product recovery by gas stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanol productivity [t/y]</td>
<td>50,000</td>
<td>91,225</td>
</tr>
<tr>
<td>Energy requirement for distillation [kgB/h]</td>
<td>2,915.73</td>
<td>6,013.60</td>
</tr>
<tr>
<td>Energy requirement for gas stripping [kgB/h]</td>
<td>-</td>
<td>8832.47</td>
</tr>
<tr>
<td>Total energy requirement [kgB/h]</td>
<td>2,915.73</td>
<td>14,846.07</td>
</tr>
<tr>
<td>Total specific energy requirement [kgB/kgB]</td>
<td>0.47</td>
<td>1.29</td>
</tr>
</tbody>
</table>

Process simulations for the traditional batch fermentation scheme have been performed for a 50,000 t/y butanol production plant [11], as representative of a retrofit of a bioethanol plant. Here the energy consumption is due to the heat duty at the beer column, water and butanol columns, to the pumps and to the vacuum pumps required to get the required void in the acetone and ethanol columns. With this
configuration of the distillation train, the total specific energy requirement is equal to 0.47 kg of butanol per kg of butanol produced.

Considering the integrated process, the continuous product removal from the fermenter allows to reduce the fermentation time by 50%, as previously stated. Therefore, the process productivity, considering the same reactor volume used in the previous scheme, is almost double. The specific consumption of the distillation train slightly increases from 0.47 kgB/kgB of the batch process to 0.52 kgB/kgB. In fact, even if the condensate obtained downstream of gas stripping undergoes a phase separation, the flowrate of the generated organic phase that can bypass the beer column is almost negligible and does not have a significant impact on the energy requirement of the train. Also, the aqueous phase obtained by mixing the aqueous phase of the condensate with the broth remaining in the reactor at the end of the fermentation exhibits a lower solvents concentration (as reported in Table 7) with respect to the batch case (Table 5). This can be explained considering that gas stripping has a low selectivity and removes, together with butanol, a large amount of water from the fermenter. At the same time, the specific energy input for the gas stripping process is high and equal to 0.77 kgB/kgB. This essentially consists of the duty required at the condenser for solvents recovery from the gas stream, due to the low concentration of ABE in the recovered stream and the associated difficulty of separating them from the gas stream. As a result, for the integrated recovery process by gas stripping, the total specific energy requirement is, therefore, higher and equal to 1.29 kgB/kgB. These results suggest that the consumption of the integrated process is almost three times greater than the traditional batch process, as also confirmed by Outram et al. [11].

In conclusion, the application of an integrated recovery process allows to increase the process productivity, but at the expense of an increase in the whole process energy demand.

7. Conclusions

Over the years, many separation techniques have been proposed or developed to mitigate the problem of product inhibition which affects the ABE fermentation process. Among them, gas stripping is considered as a viable solution for that.

This work has focused on its application to a classical batch fermenter, to evaluate the advantages it offers and the possible drawbacks. To accomplish that, the fermentation process has been integrated with the gas stripping unit by solving material balance equations which involve some removal functions to take into account the withdrawal of the fermentation broth from the reactor and its processing in the stripping column. The two liquid phases which are formed by cooling down the vapor stream leaving the stripping column have been further treated in a five-column distillation train. The same downstream scheme has been also considered for the recovery of the solvents from the
broth remained in the reactor at the end of a classical batch fermentation process (thus not integrated with the gas stripping unit), in order to compare the two process solutions. To account for the energy requirements of each of them, an energy analysis has been performed on the basis of the net equivalent fuel approach.

The obtained results have suggested that the application of gas stripping as integrated recovery technique allows to increase the process productivity, but at the expense of an increase in the whole process energy demand. It may be interesting to carry out the comparison also considering other possible operation modes for both the reactor and the gas stripping recovery technique.

Nomenclature

**Acronyms**

- **ABE**: Acetone-Butanol-Ethanol
- **COP**: Coefficient of Performance
- **EoS**: Equation of State
- **LHV**: Lower Heating Value [MJ/kg]
- **LLE**: Liquid-Liquid-Equilibrium
- **LP**: Low-pressure
- **NRTL**: Non-Random Two-Liquid
- **RK**: Redlich-Kwong
- **VLE**: Vapor-Liquid-Equilibrium

**Symbols**

- $a_{ij}$: Binary interaction parameter of the NRTL-RK model
- $a_k$: Coefficients in the definition of $m_A$ ($k = 1, 2$) and $q_A$ ($k = 3, 4, 5$)
- $b_{ij}$: Binary interaction parameter of the NRTL-RK model
- $b_k$: Coefficients in the definition of $m_B$ ($k = 1, 2$) and $q_B$ ($k = 3, 4, 5$)
- $C$: Concentration, [g/L]
- $D_f$: Dilution factor, [1/h]
- $e_k$: Coefficients in the definition of $m_E$ ($k = 1, 2$) and $q_E$ ($k = 3, 4, 5$)
- $f$: Functions defined in Eqs. (1)-(2)
- $m_j$: Coefficients in the removal functions ($j = A, B, E, WB$)
- $m$: Mass [kg]
- $\dot{m}$: Flow rate, [kg/s]
- $P$: Pressure, [atm]
- $Q$: Duty, [kW]
- $q_j$: Coefficients in the removal functions ($j = A, B, E, WB$)
- $R^2$: Coefficient of determination
- $r$: Reaction rate, [g/L/h]
- $T$: Temperature, [K]
- $t$: Time, [h]
- $V_F$: Fermenter volume [L]
- $\dot{W}_{el}$: Electric power, [kW]
- $w_{bk}$: Coefficients in the definition of $m_{WB}$ ($k = 1, 2$) and $q_{WB}$ ($k = 3, 4, 5$)
- $x$: Mole fraction, [-]
Greek symbols

\(\alpha\) Non-randomness parameter of the NRTL-RK model

\(\eta_{\text{boiler}}\) Boiler efficiency, [-]

\(\eta_i\) Removal function for \(i\)-th component, [-]

\(\eta_{\text{CC}}\) Combined-cycle efficiency, [-]

\(\eta_{\text{II}}\) Second principle efficiency, [-]

Subscripts

\(A\) Acetone

\(B\) Butanol

\(ba\) Butyric acid

\(\text{cold}\) Cold reservoir

\(E\) Ethanol

\(F\) Referred to the fermenter/end of the fermentation

\(FUEL\) Referred to the fuel

\(\text{hot}\) Hot reservoir

\(i\) \(i\)-th component

\(R\) Referred to a refrigeration cycle

\(R_{\text{id}}\) Referred to an ideal Carnot cycle

\(S\) Referred to stripped components

\(W\) water

References


Figure 1. Comparison between VLE and LLE experimental data [16-23] for the system water-butanol (P = 1 atm) and prediction by the Aspen Plus® [15] NRTL-RK model with default (dotted line) and regressed (solid line) parameters.

Figure 2. LLE experimental data (symbols from [24]) for the system acetone-water-butanol and prediction by the Aspen Plus® [15] NRTL-RK model with default parameters (dotted line) and with regressed parameters (solid line) at a temperature of: a) 293.15 K; b) 313.15 K.

Figure 3. LLE experimental data (dots from [25]; triangle down from [16]) for the system ethanol-water-butanol and prediction by the Aspen Plus® [15] NRTL-RK model with regressed parameters (solid line) at 298.15 K.

Figure 4. Scheme of the integrated fermenter-stripping process.

Figure 5. Scheme of the distillation train used for the ABE separation downstream of the integrated fermentation-stripping process (green arrows denote electrical energy requirements, red arrows denote heat duties, blue arrows denote cooling duties).

Figure 6. Concentration profiles obtained from the modeling of the batch fermentation process: (— · —, violet) sugar, (∙∙∙∙, black) biomass, (— – –, light blue) acetic acid, (— – –, orange) butyric acid, (— —, green) acetone, (— —, red) butanol, (— —, blue) ethanol.

Figure 7. Concentration profiles obtained from the modeling of the integrated fermenter-gas stripping process: (— · —, violet) sugar, (∙∙∙∙, black) biomass, (— – –, light blue) acetic acid, (— – –, orange) butyric acid, (— —, green) acetone, (— —, red) butanol, (— —, blue) ethanol. The vertical dotted line indicates when the gas stripping starts.

Figure 8. Profiles of mass flowrates removed from the fermenter during the integrated fermenter-gas stripping process: (— – –, light blue) water, (— —, green) acetone, (— —, red) butanol, (— —, blue) ethanol. The vertical dotted line indicates when the gas stripping starts.