

Synthesis and design of new hybrid configurations for biobutanol purification

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ABSTRACT

The development of new technologies for biobutanol production by fermentation has resulted in higher butanol concentrations, less by-products and higher volumetric productivities during fermentation. These new technology developments have the potential to provide a production process that is economically viable in comparison to the petrochemical pathway for butanol production. New alternative hybrid configurations based on liquid–liquid extraction and distillation for the biobutanol purification were presented. The alternatives are designed and optimized minimizing two objective functions: the total annual cost (TAC) as an economical index and the eco-indicator 99 as an environmental function. All the new configurations presented reduced the TAC compared to the traditional hybrid configuration, in particular a thermally coupled alternative exhibited a 24.5% reduction of the TAC together with a 11.8% reduction of the environmental indicator. Also intensified sequences represented a promising option in the reduction of the TAC but with some penalty in the eco-indicator.

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1. Introduction

Butanol is a clear, colorless liquid alcohol widely used as a solvent, as a chemical intermediate, in cosmetic products, in drugs and in many other applications. After 2005, when David Ramey drove from Ohio to California and back his unmodified car, using 100% butanol, the interest in developing an efficient and sustainable butanol production process has raised due to its possible employ as gasoline additive as well as a fuel (Dürre, 2007).

The production of butanol through anaerobic bacteria fermentation of starchy substrates has been reported by Pasteur in 1862. Acetone, butanol and ethanol are the main compounds obtained; the process is usually referred as ABE fermentation, and the butanol produced is called biobutanol.

The considerable request of acetone during World War 1 and 2 and the isolation of high solvent yield strains patented by Weizmann (1916) makes ABE fermentation the second largest bio-process ever performed. Until 1950, two-thirds of the total butanol production came from biological processes (Dürre, 2007). In the

post-war years the simultaneous increasing of the substrate cost, the huge amounts of effluents produced during the fermentation and most of all, the growing of the new petrochemical industry, has settled forth the decreasing of the ABE fermentation process (Gibbs, 1983).

Nowadays butanol is mainly produced as a petro-derived by catalytic hydroformylation of propylene and hydrogenation of the formed aldehydes; this process is known as oxo-synthesis (Matar and Hatch, 2001). Since its production is related to the propylene availability, butanol profitability is deeply related to the crude oil price fluctuations.

The overconsumption of petro-derived products and the necessity to reduce the greenhouse gas emissions, particularly the ones related to the transport sector, has catalyzed the interest in developing bio-derived fuels, like bioethanol and biodiesel. The transition between non-renewable energy sources and biofuels is also promoted by political actions and different guidelines are given, as for example by the European Parliament (Directive, 2003/30/EC, 2003).

Compared to other biofuels like bioethanol, biobutanol has different benefits. It has a higher energy density, it has a lower vapor pressure, it is less corrosive, it is not hygroscopic and it can be blended in any concentration with gasoline or used as a pure fuel without any change in car's engines (Dürre, 2007; Swana

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et al., 2011). For all these reasons the ABE fermentation process has been reconsidered as a valid alternative to produce bioderived butanol. However, it is necessary to improve the ABE fermentation in a way that the process becomes not only environmental friendly, but also economically competitive if compared to the petroleum-based synthetic route. To bridge the gap between the fermentation-derived and the petroleum-based butanol, some open issues should be analyzed.

First it is necessary to identify cheap waste materials suitable for the fermentation. It is generally accepted that non-food competitive feedstocks should be used as a source of sugars, and agricultural wastes are an appropriate solution (Chen et al., 2012; Kumar et al., 2012). Another crucial point is the strains development. Butanol is toxic for the culture cells, subsequently the substrate must be diluted and the correspondent yield of butanol is low. Comparing the total solvents concentration (acetone, butanol and ethanol) of 20 g L^{-1} obtained with traditional strains, it is possible to produce up to 33 g L^{-1} solvents by hyper-butanol-producing strain (Qureshi and Blaschek, 2001). Efficient genetic engineering tools are essential to realize competitive biobutanol productions. Another valid alternative to increase the butanol yield is the improvement of fed-batch or continuous processes (Mariano et al., 2011; Mariano, 2010; Roffler et al., 1988). Finally an energy efficient product recovery section is essential for the convenience of the production. It is normally required that the energy used for the butanol separation must be lower than the energy content of the product itself (Qureshi et al., 2005). Different separation alternatives have been explored in the literature. Adsorption of butanol onto the surface of a suitable adsorbent material is considered one of the most energy efficient separation techniques (Yang et al., 1994). Anyway, since now, has been tested only on laboratory scale and seems not suitable for industrial applications (Kaminski et al., 2011). If pervaporation is considered as purification method, the separation is realized by the partial vaporization of the mixture through a membrane. At the present time most of the studies are focused on exploring different membrane performances (Jee and Lee, 2014). Gas stripping is a very common separation technique where an oxygen-free carrier gas is bubbled in the fermentor; acetone, butanol, ethanol and water are stripped away increasing the butanol yield of the system (Ezeji et al., 2005). Liquid–liquid extraction is another possibility of great interest among all the other possibilities. It is performed adding an organic water-immiscible extractant to the fermentation broth. The organic phase containing butanol and other products are then removed and sent for the extractant recovery and product separation. In order to avoid the possibility in microorganisms extractant poisoning, the extraction is usually performed in an external column (Dadgar and Foutch, 1988; Roffler et al., 1987). When distillation is considered, the presence of azeotropes in the mixture makes the separation difficult and energy demanding. It was estimated that for a butanol concentration of 1 wt% the energy required for the butanol separation equals 1.5 times the energy content of butanol itself. But if the butanol concentration raises to 4 wt% the amount of energy requested decreases to 0.25 (Ezeji et al., 2004). Further details about the cited methods can be found in the review work of Abdehagh et al. (2014). The present work is focuses on exploring different separation alternatives for the ABE separation proposing new configurations. Moreover a synthesis procedure method that allows the designer to explore a wide set of separation alternatives is presented. The new configurations proposed are compared for their total annual costs and environmental impact.

2. Separation flowsheets based only on distillation

Talking about separations, distillation is for sure the first option to be considered. Even if many alternatives have been proposed

in order to reduce the energy consumption or the capital investment, distillation is the industrial favored unit operation (Keller and Bryan, 2000).

Considering the ABE mixture, the presence of the ethanol–water homogeneous azeotrope and the butanol–water heterogeneous azeotrope, makes the separation challenging. Marlatt and Datta (1986) introduced the ABE separation sequence reported in Fig. 1(a). This sequence, based on distillation, is composed by three columns and two strippers. The fermentation broth is sent to the first column, usually called broth distillation still or beer stripper, where butanol, acetone and 90% of the ethanol are recovered in the distillate. This stream is fed to the second distillation column referred to as ABE still, the distillate flows to the third distillation column for the acetone–ethanol separation. The bottoms stream of the ABE still is sent to a decanter, both aqueous and butanol rich phases are stripped and the vapors recycled back to the decanter. Water and butanol are obtained from the strippers. Recycle water is also produced as residue from the broth still.

A similar configuration, but with two columns dedicated to the acetone–ethanol separation was reported by Roffler et al. (1987).

More recently Kraemer et al. (2011) proposed a pure distillation process composed by four columns as reported in Fig. 1(b). In the first column all the butanol, acetone and ethanol are recovered in the distillate with some water also. This column is equipped with a decanter and the butanol rich stream is fed to the second column where acetone is recovered as distillate. The bottoms stream proceeds to the decanter where the butanol rich phase is fed to the third column to separate the ethanol–water azeotropic mixture and finally the last column is dedicated to the purification of butanol.

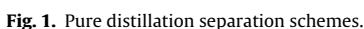
As extensively highlighted in the literature and as already mentioned, pure distillation processes are proved to be not competitive for this kind of separation (Dadgar and Foutch, 1988; Roffler et al., 1987; Kraemer et al., 2011; Liu et al., 2004; van der Merwe et al., 2013), but there is still the convenience to combine distillation in hybrid flowsheets with other unit operations.

In the present work pure distillation sequences are considered only for comparison purpose.

3. Hybrid extraction–distillation processes

The combination of extraction and distillation is considered as one of the most promising separation alternatives for the ABE purification (Dadgar and Foutch, 1988; Roffler et al., 1987; Kraemer et al., 2011; van der Merwe et al., 2013; Sanchez Ramirez, 2015). This hybrid flowsheet was also successfully applied to the purification of bioethanol using a combination of liquid–liquid extraction and extractive distillation (Avilés Martínez et al., 2012). The extraction column is located after the fermentor, the mass separation agent or extractant, is fed from the bottom and the fermentation broth from the top. The raffinate phase contains water and traces of acetone, butanol and water. The extract phase contains the extractant, acetone, butanol and ethanol. The selection of the extractant is of meaningful importance for the economy of the process because directly affects the composition of the extract phase. Different researches are focused on the solvent screening (Kraemer et al., 2011; Oudshoorn et al., 2009) and it is possible to generalize that a good extractant, besides its economicity and low toxicity, should have a high distribution coefficient for the butanol and a high selectivity between butanol and water.

The extract phase obtained from the extractor is feed to the distillation section where acetone, butanol and ethanol can be recovered following different arrangements employing simple and/or complex columns. The liquid–liquid extraction may eliminate the request of azeotropic distillation making the process more competitive compared to pure distillation flowsheets.



Not so many works have been focused on the synthesis of alternative flowsheets for the ABE separation. The work of [Liu et al. \(2004\)](#) represents an exception since explored different process alternatives based on distillation and liquid–liquid extraction. The generation of all the alternatives was obtained applying the graph-theoretic method based on P-graphs ([Friedler et al., 1992](#)). It was clearly evidenced that only hybrid flowsheet are competitive in terms of total annual cost. The configuration selected with the lowest value of total annual cost is reported in [Fig. 2](#). The flowsheet is composed by a liquid–liquid extraction column followed by three distillation columns, the first performs the solvent recovery and the last two are for the products purification. This type of distillation sequence, referred as Complex-Direct, was also discussed by [Doherty and Malone \(2001\)](#) proving its convenience for some other mixtures. The peculiarity of this distillation sequence is represented by the column that performs the separation acetone/ethanol–butanol. This column is classified as a complex column since it has one side stream. Both the side and the bottom streams are composed by a mixture of ethanol and butanol that are fed to the third column. The configuration reported in [Fig. 2](#) represents the reference sequence used for the alternatives generation. The methodology used to predict the alternative

Fig. 2. Hybrid L-L and distillation reference configuration.

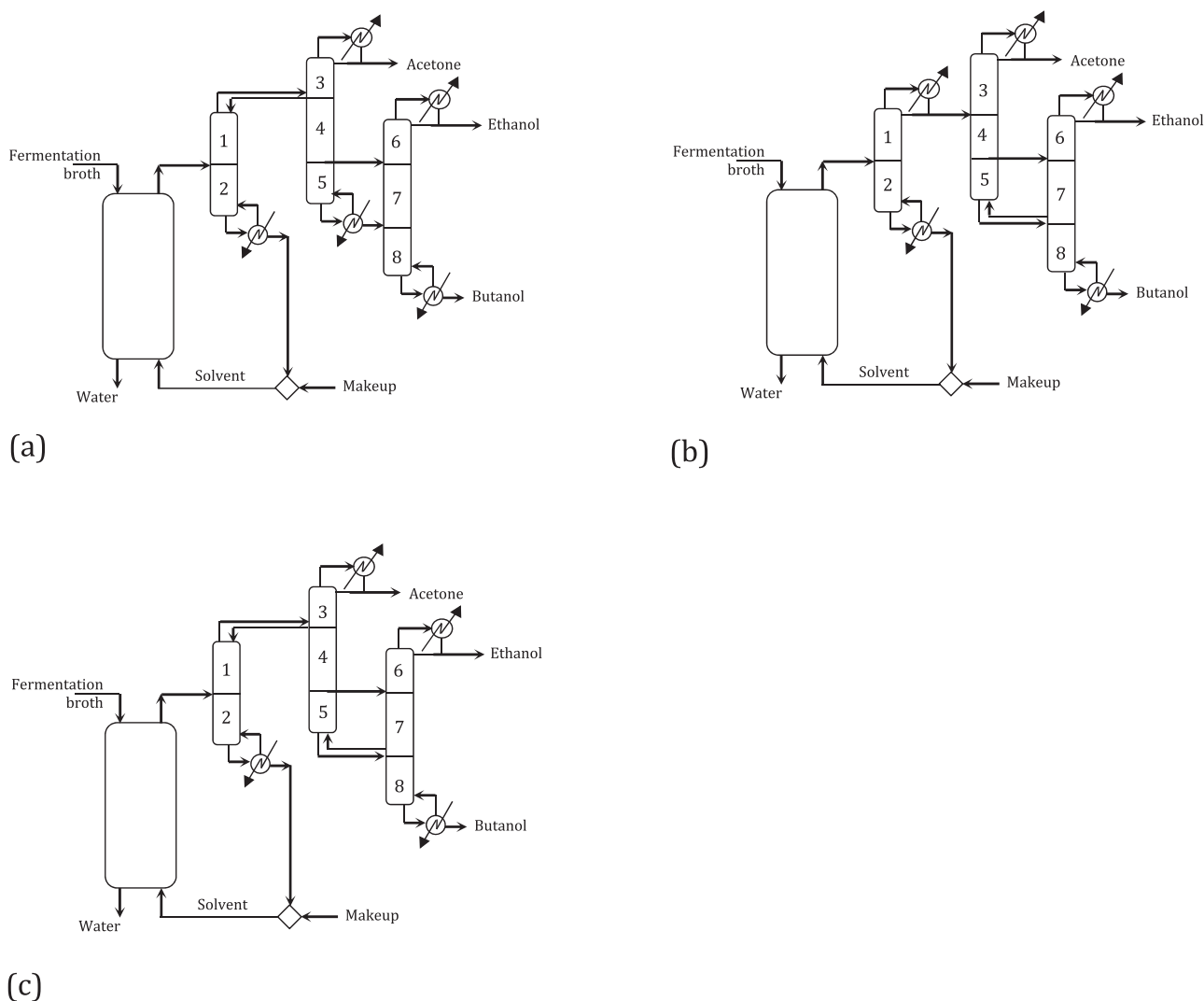


Fig. 3. Thermally coupled alternatives.

4.1. Alternative thermally coupled configurations

Starting from the reference configuration of Fig. 2 it is possible to obtain the three thermally coupled sequences reported in Fig. 3. One or more thermal couplings have been introduced in correspondence to condensers and/or reboilers associated to non-product streams. In this way the configuration of Fig. 3(a) was obtained by substitution of the solvent recovery column condenser with a thermal coupling. In Fig. 3(b) the reboiler of the second distillation column was substituted with a thermal coupling and in Fig. 3(c) both condenser and reboiler have been removed.

4.2. Thermodynamically equivalent alternative configurations

Every time a thermal coupling is introduced, there is a column sections where the condenser and/or the reboiler provides a common reflux ratio and/or a common vapor boil-up between two consecutive columns. Moving this column section it is possible to generate the thermodynamically equivalent alternatives reported in Fig. 4. Five combinations are possible. Fig. 4(a) was obtained from the corresponding thermally coupled sequence of Fig. 3(a) moving section 3 above section 1. Following the same procedure, Fig. 5(b) was generated moving section 8 below section 5. Configurations

shown in Fig. 4(c–e) are obtained from the corresponding sequence in Fig. 3(c), where the presence of two thermal couplings makes sections 3 and 8 simultaneously movable.

4.3. Intensified alternative configurations

The intensified sequences are those that performed a defined separation task with a reduced number of equipment compared to the traditional configurations. The procedure to generate the intensified sequences started from the thermodynamically equivalent configurations by elimination of single column sections defined as transport sections (Errico and Rong, 2012; Errico et al., 2009). In this particular case the thermodynamically equivalent sequences of Fig. 4 do not contain single column sections because of the presence of the side stream. Anyway the side stream is not associated to the separation of a product stream and the corresponding column section can be eliminated to generate the new sequences reported in Fig. 5. For instance, the configuration shown in Fig. 5(a) was obtained from the corresponding sequence of Fig. 4(a) by elimination of sections 4 and 5 and connecting the solvent recovery column to the ethanol/butanol separation column. The same principle has been used for the sequences in figures (b–e).

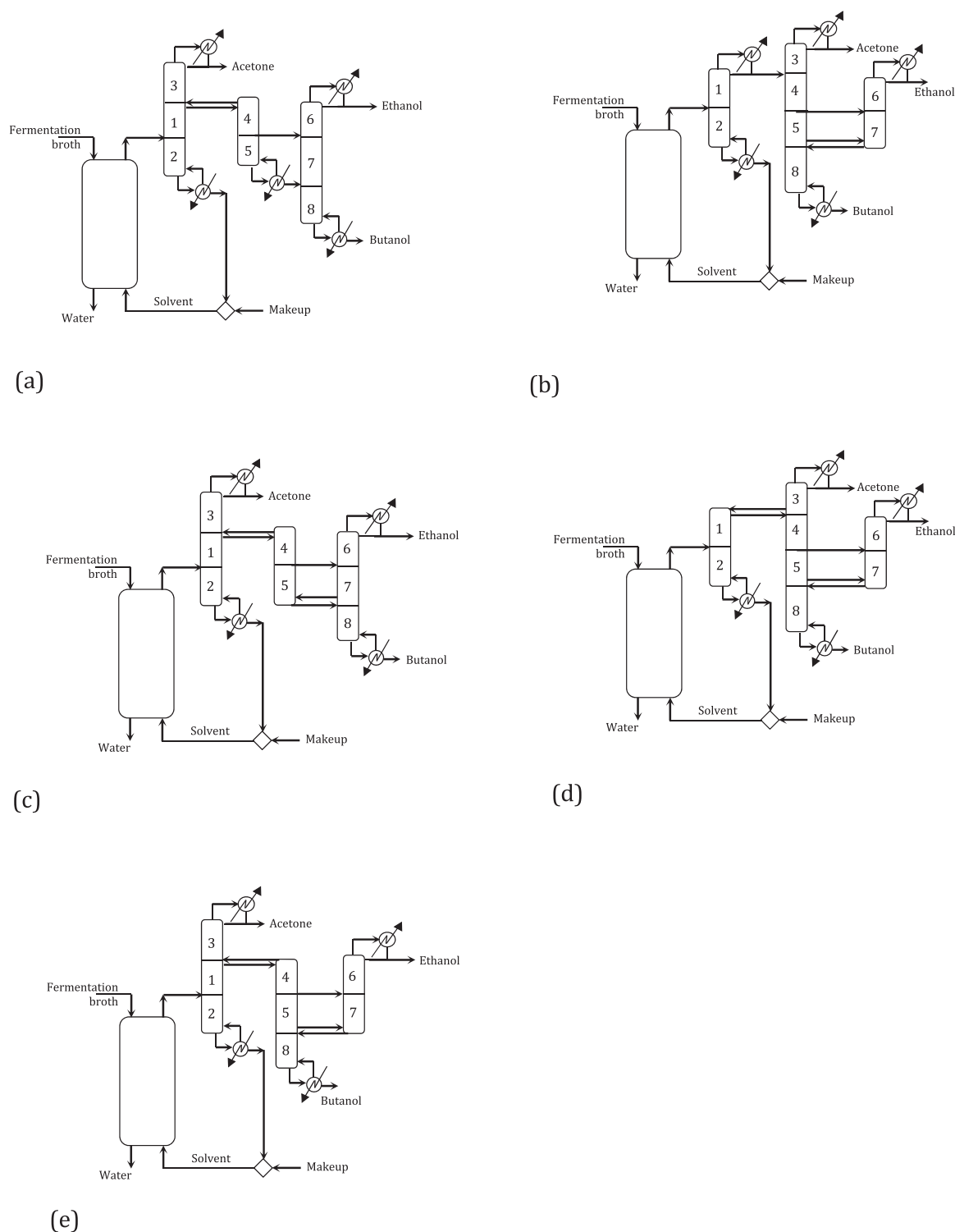


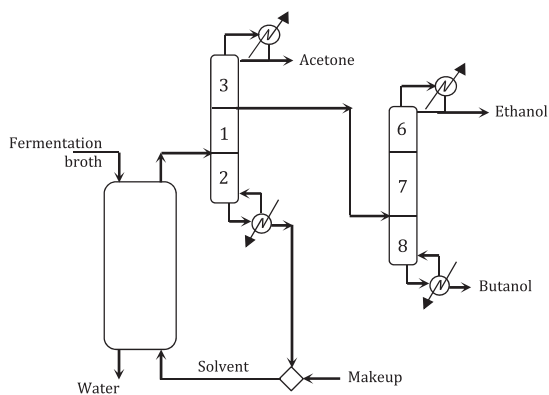
Fig. 4. Thermodynamic equivalent configurations.

5. Design and simulation of the new alternative biobutanol configurations

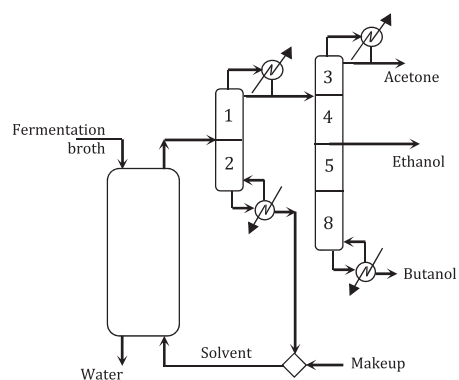
In order to test the convenience of the proposed sequences, the alternatives were simulated by means of Aspen Plus V8.0.

The first step in the simulation of the new separation alternatives, is the definition of the feed components. In Table 1 some of the most meaningful results on this topic have been summarized. It

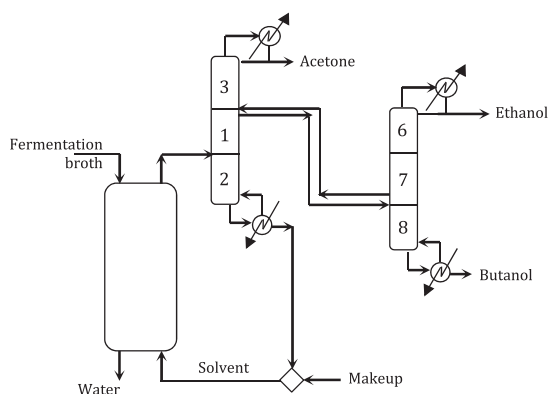
is possible to notice that a very mottled distribution of concentrations is reported by various authors. These results were expected since the broth composition mainly depends on the process' type (batch or continuous) and on the fermentation strains used. It is also reasonable that the research on this topic is mainly focused in developing alternatives to increase the yield of butanol in the fermentation broth in order to make the whole process competitive or even better than the corresponding petro-derived butanol. Following this trend, the broth composition, used to model all



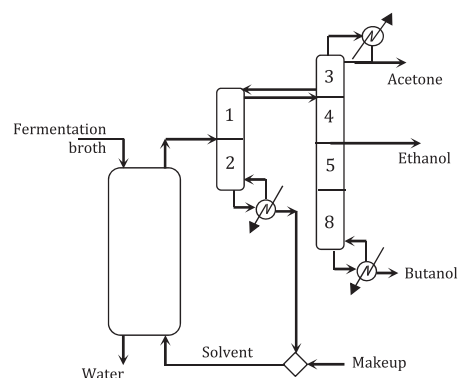
(a)



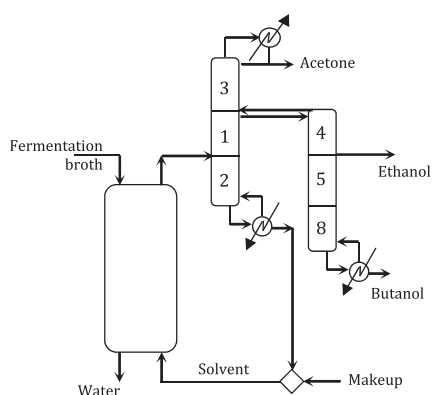
(b)



(c)



(d)



(e)

Fig. 5. Intensified configurations.

the new separation alternatives, was chosen according to the last developing on the topic (Wu et al., 2007). The feed physical parameters and the composition are reported in Table 2.

According to the indications of van der Merwe et al. (2013) the NRTL-HOC thermodynamic model was selected for all

the simulations. Hexyl acetate was chosen as solvent in the liquid–liquid extractor.

The minimum purity targets are 99.5 wt% for biobutanol, 99.5 wt% for acetone and 95.0 wt% for the ethanol. Only when stand-alone distillation is considered as separation method, the

Table 1
Separation unit feed composition comparison.

Author	Butanol	Acetone	Ethanol	Acetic acid	Butyric acid
Roffler et al.	40 (g L ⁻¹)	22 (g L ⁻¹)	6 (g L ⁻¹)	–	–
Ezeij et al.	151.7 (g L ⁻¹)	77.7 (g L ⁻¹)	3.4 (g L ⁻¹)	4.3 (g L ⁻¹)	4.2 (g L ⁻¹)
Roffler et al.	21.0 (g L ⁻¹)	3.5 (g L ⁻¹)	0.4 (g L ⁻¹)	–	–
Marlatt and Datta	1.5 (wt%)	0.6 (wt%)	0.2 (wt%)	0.18 (wt%)	0.08 (wt%)
Kraemer et al.	8 (g L ⁻¹)	10.5 (g L ⁻¹)	5 (g L ⁻¹)	–	–
Wu et al.	42.728 (lb h ⁻¹)	23.997 (lb h ⁻¹)	1.032 (lb h ⁻¹)	–	–

Table 2
Feed characterization.

Temperature (K)	322.0390
Vapor fraction	0
Flowrate (kg h ⁻¹)	45.3592
Composition (wt%)	
Butanol	0.3018
Acetone	0.1695
Ethanol	0.0073
Water	0.5214

maximum purity achievable for the ethanol was below the fixed threshold. The column pressure was optimized to allow the use of cooling water in the condensers. The reference and the alternative sequences have been designed minimizing simultaneously two objective functions; the total annual cost and an environmental index. The functions and the optimization method are described as follow.

5.1. Economic objective function

The minimization of the total annual cost (TAC) is the index considered for the economic evaluation of the alternatives.

$$\text{TAC} = \frac{\text{Capital costs}}{\text{Payback period}} + \text{Operative costs} \quad (1)$$

The minimization of this objective function is subject to the required recoveries and purities in each product stream, i.e.:

$$\begin{aligned} \text{Min (TAC)} &= f(N_{\text{tn}}, N_{\text{fn}}, R_{\text{rn}}, F_{\text{rn}}, F_{\text{vn}}, F_{\text{ln}}, D_{\text{cn}}) \\ \text{Subject to } \bar{y}_m &\geq \bar{x}_m \end{aligned} \quad (2)$$

where N_{tn} are total column stages, N_{fn} is the feed stages of all streams in column, R_{rn} is the reflux ratio, F_{rn} is the distillate flowrate, F_{vn} is the vapor flow in thermally coupled configurations, F_{ln} is the liquid flow in thermally coupled configurations and D_{cn} is the column diameter, y_m and x_m are vectors of obtained and required purities for the m components, respectively. The capital costs were evaluated in function of the units capacity following the procedure reported by Turton et al. (2009). Sieve tray distillation columns equipped with fixed tube condensers and floating head kettle reboiler were considered. For the distillation columns the number of theoretical stages was converted to actual stages using the overall efficiency expression developed by Lockett (Peters et al., 2004). For the liquid–liquid extractor, the efficiency was evaluated according to the modified Treybal's correlation (Krishna Murty and Rao, 1968). A payback period of 5 years was considered for all the cases considered. The cost of the solvent flowrate was not included in the TAC calculation since no significant differences among the configurations were evidenced. The minimization of the TAC implies the manipulation of a maximum of 25 continuous and discrete variables. For each configuration considered, the complete list of variables is provided as [Supplementary Material in Table S1](#). Note that, since the product streams flows are manipulated, the recoveries of the key components in each product stream must be included as a restriction in the optimization problem.

5.2. Environmental objective function

The environmental impact is measured through the eco-indicator 99, based on the methodology of the life cycle analysis introduced by Geodkoop and Spriensma (2001) and stated as follows:

$$\text{Min(Eco-indicator)} = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (3)$$

where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused in category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d , and δ_d is the normalization factor for damage of category d .

In the eco-indicator 99 methodology, 11 impact categories are considered (Geodkoop and Spriensma, 2001)

1. Carcinogenic effects on humans.
2. Respiratory effects on humans that are caused by organic substances.
3. Respiratory effects on humans caused by inorganic substances.
4. Damage to human health that is caused by climate change.
5. Human health effects that are caused by ionizing radiations.
6. Human health effects that are caused by ozone layer depletion.
7. Damage to ecosystem quality that is caused by toxic emissions in the ecosystem.
8. Damage to ecosystem quality that is caused by the combined effect of acidification and eutrophication.
9. Damage to ecosystem quality that is caused by land occupation and land conversion.
10. Damage to resources caused by the extraction of minerals.
11. Damage to resources caused by extraction of fossil fuels.

These 11 categories are aggregated into three major damages categories: (1) human health, (2) ecosystem quality, and (3) resources depletion.

5.3. Optimization strategy

In order to optimize the alternative configurations developed for the biobutanol configuration, a multi-objective optimization method was used. This multi-objective optimization strategy is an evolutionary method based on the combination of differential evolution (DE) and tabu meta-heuristics. In particular, the differential evolution method was proposed by Storn and Price (1997) in order to solve single objective optimization problems over continuous domain. Subsequently, Abbas et al. (2001) and Madavan (2002) adapted DE for solving multi-objective optimization (MOO) problems. Basically, DE algorithm consists of three steps: generation, evaluation, and selection. Generation involves the production of new individuals via mutation and crossover operators, whereas the fitness value (related to the objective function) of each individual of the new population is calculated. The selection permits only those individuals who exhibited better fitness values to advance to the next generation. All those steps will be repeated until the better fitness values are found or a specified

amount of generations are accomplished. On the other hand, the Taboo search (TS) was proposed by Glover (1989) for combinatorial optimization. Taboo algorithm allows keeping the record of recently visited points to avoid further revisit of explored areas. In particular, Srinivas and Rangaiah (2007) used the concept of taboo list (TL) with DE to avoid the evaluation of the same point in the search space and developed a powerful hybrid stochastic optimization method (DETL). This characteristic improves the performance and decreases the computational time for global optimization. This algorithm has been extended by Sharma and Rangaiah (2013) for handling multi-objective optimization problems with promising results. The multi-objective differential evolution with tabu list (MODE-TL) algorithm handles inequality constraints by feasibility approach of Deb (2011). Results reported by Sharma and Rangaiah (2010) showed that MODE-TL is reliable for solving multi-modal optimization problems due to the synergic performance caused by the integration of multi-objective DE with TL. Further, MODE-TL have been used in many knowledge sectors, i.e., Bonilla-Petriciolet et al. (2013) handled phase equilibrium data in order to estimate thermodynamic parameters and data reconciliation in phase equilibrium modeling. MODE-TL has good convergence characteristics confirmed by the tests performed by Bonilla-Petriciolet et al. (2013) in highly non-convex surfaces such as modeling of activity coefficients of aqueous electrolytes.

The implementation of the optimization algorithm was made by a hybrid platform using Microsoft Excel and Aspen Plus. The vector of decision variables (i.e., the design variables) are sent to Microsoft Excel using dynamic data exchange (DDE) through COM technology. In Microsoft Excel, these values are attributed to the process variables that Aspen Plus needs. After the simulation it is completed, Aspen Plus returns to Microsoft Excel the resulting vector. Finally, Microsoft Excel analyzes the values of the objective functions and proposes new values of the decision variables according to the stochastic optimization method. The following parameters for the DETL method have been used: 200 individuals, 300 generations, a tabu list of 50% of total individuals, a tabu radius of 2.5×10^{-6} , 0.80 and 0.6 for crossover and mutation fractions, respectively. These parameters were obtained from the literature and through a tuning process via preliminary calculations (Srinivas and Rangaiah, 2007). The tuning process consists of performing several runs with different number of individuals and generations in order to detect the best parameters to improve the convergence performance of DETL.

6. Optimization results

In this section, the results obtained for the different alternatives are reported and compared in order to select the optimal configuration.

6.1. Distillation based configurations

A direct comparison between the two alternatives presented in Fig. 1(a) and (b) cannot be easily done since there are some differences in the maximum purity achieved by the products. In the flowsheet of Fig. 1(a) the ethanol is obtained with a purity of 93.05 wt% due to the azeotrope limitation; moreover, two pure water streams are produced, one as bottom stream in the first column and one from the stripper aqueous phase connected to the decanter. On the whole, 100% of acetone and butanol, 99.68% of water and 99.08% of ethanol are recovered in the configuration of Fig. 1(a).

In the flowsheet reported in Fig. 1(b), the ethanol is not recovered at high concentration but only 51.63 wt% is reached in the third column's distillate. Pure water is recovered only from the first column. Two waste streams are obtained; one from the decanter and

Table 3

Total annual cost and eco-indicator 99 for the configurations of Figs. 1, 3, 4 and 5.

Configuration	TAC (\$ y ⁻¹)	Eco-ind. (points y ⁻¹)
1(a)	1,061,581	17,729
1(b)	1,030,870	16,685
2	234,172	13,017
3(a)	214,280	12462
3(b)	212428	13350
3(c)	188143	11642
4(c)	189102	12017
4(d)	188471	11571
4(e)	184930	11894
5(c)	198160	19684
5(d)	168490	16681
5(e)	163631	15595

one from the distillate of the fourth column. Only 54.61% and 38.15% of water and ethanol are recovered respectively. Better results are obtained for the acetone, since 99.98% is recovered; for the butanol that represents the main product, 68.37% is recovered in the flow-sheet considered.

Since these configurations are introduced only to prove the convenience to use hybrid configurations, the detailed design is reported only as Supplementary Material in Tables S2 and S3. The results for the TAC and the eco-indicator are showed in Table 3. It is possible to notice that configuration 1(b) has a TAC 2.98% less than the flowsheet 1(a), even if, as evidenced before, ethanol is not recovered to a useful concentration, different waste streams are produced and the product recoveries are lower compared to the configuration reported in Fig. 1(a).

6.2. Reference hybrid liquid–liquid and distillation structure

The configuration reported in Fig. 2 represents the reference for the comparison with all the alternatives. The detailed design together with the energy consumption is reported in Table 4. Vapor phase is considered for the side stream connecting the second and the third column. Acetone was recovered with a purity of 99.78 wt%, 95.95 wt% for the ethanol and 99.92 wt% for the butanol. The TAC value of the hybrid L–L configuration is less than a quarter compared to the best distillation alternative; moreover, a 36% reduction of the eco-indicator is also observed according to the data reported in Table 3. It is clear that flowsheets based only on distillation are not competitive due to the lower purity obtained in the ethanol stream, the amount of waste streams generated, the low recovery, the value of the total annual cost and finally also the eco-indicator.

6.3. Thermally coupled configurations

The thermally coupled configurations shown in Fig. 3 are here considered for their potential in energy reduction. The three

Table 4

Design parameters and comparison indexes for the reference configuration of Fig. 2.

	Extractor	C1	C2	C3
Number of theoretical stages	5	26	46	20
Overall efficiency	0.654	0.766	0.721	0.834
Reflux ratio	–	0.905	6.034	14.836
Feed stage	1	13	32	5/15
Solvent feed stage	5	–	–	–
Side stream stage	–	–	44	–
Column diameter (m)	0.335	0.322	0.325	0.292
Operative pressure (kPa)	101.353	101.353	101.353	101.353
Distillate flowrate (kg h ⁻¹)	–	21.687	7.694	0.333
Side stream flowrate (kg h ⁻¹)	–	–	1.901	–
Solvent flowrate (kg h ⁻¹)	708.549	–	–	–
Solvent makeup (kg h ⁻¹)	0.709	–	–	–
Condenser duty (kW)	–	7.284	7.736	1.239
Reboiler duty (kW)	–	65.919	8.428	0.907

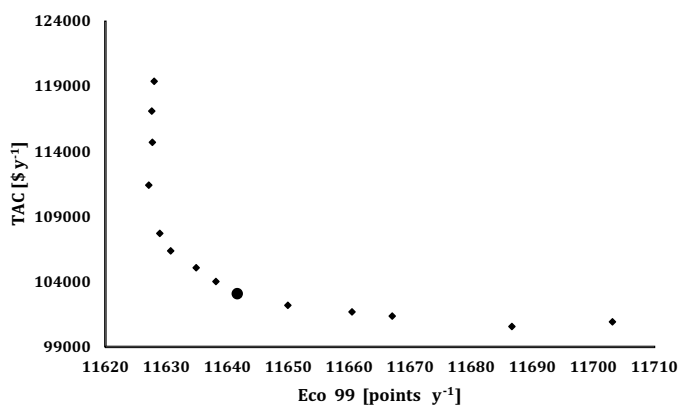


Fig. 6. Pareto-optimal solutions for the configuration of Fig. 3(c).

alternatives are compared for the economic and environmental performance in Table 3. It is possible to notice that from an economic point of view, all the options have a lower value of the TAC compared to the reference configuration. In particular, the best thermally coupled configuration is the one reported in Fig. 3(c), obtained removing the condenser of the first column and the reboiler of the third one. In this case, the TAC is 24.5% less and the eco-indicator 11.8% lower compared to the base hybrid configuration of Fig. 2. Fig. 6 shows the pareto-optimal solutions, where it is possible to notice the competition between the objective functions. The chosen solution was marked with a circle. Regarding the eco-indicator 99, 95.63% of its value is due to the impact of the steam used in the columns reboiler, 3.24% to the electricity used and 1.13% to the construction materials. The detailed design of the best thermally coupled configuration is reported in Table 5. The design of the configurations in Fig. 3(a) and (b) is reported in Tables S4 and S5 of the Supplementary Material.

It was extensively proved that there is a correspondence among the alternatives included in the different subspaces (32, 33). It means that once the best structure is identified in a specific subspace of alternatives, only the configurations derived from that structure are expected to be promising.

For this reason, since the best thermally coupled configuration has been identified, only the alternatives derived for that configuration are considered.

Table 5
Design parameters for the thermally coupled configuration of Fig. 3(c).

	Extractor	C1	C2	C3
Number of theoretical stages	5	26	46	20
Overall efficiency	0.654	0.753	0.758	0.726
Reflux ratio	–	–	5.424	14.631
Feed stage	1	13	32	5/15
Solvent feed stage	5	–	–	–
Side stream stage	–	–	44	–
Column diameter (m)	0.335	0.321	0.325	0.287
Operative pressure (kPa)	101.353	101.353	101.353	101.353
Distillate flowrate (kg h ^{−1})	–	–	7.716	0.332
Thermal coupling flowrate (kg h ^{−1})	–	–	14.978	9.139
Side stream flowrate (kg h ^{−1})	–	–	2.900	–
Solvent flowrate (kg h ^{−1})	708.465	–	–	–
Solvent makeup (kg h ^{−1})	0.709	–	–	–
Condenser duty (kW)	–	0.000	7.096	1.214
Reboiler duty (kW)	–	65.082	0.000	2.222

Table 6

Design parameters and comparison indexes for the configuration of Fig. 5(e).

	Extractor	C1	C2
Number of theoretical stages	5	58	20
Overall efficiency	0.654	0.783	0.718
Reflux ratio	–	27.182	–
Feed stage	1	45	–
Solvent feed stage	5	–	–
Side stream stage	–	–	12
Column diameter (m)	0.335	0.323	0.324
Operative pressure (kPa)	101.353	101.353	101.353
Distillate flowrate (kg h ^{−1})	–	7.711	–
Thermal coupling flowrate (kg h ^{−1})	–	118.621	–
Side stream flowrate (kg h ^{−1})	–	–	0.336
Solvent flowrate (kg h ^{−1})	708.289	–	–
Solvent makeup (kg h ^{−1})	0.684	–	–
Condenser duty (kW)	–	31.094	0.000
Reboiler duty (kW)	–	65.642	24.517

6.4. Thermodynamically equivalent configurations

Once the configuration of Fig. 3(c) has been identified as the best thermally coupled alternative, the thermodynamically equivalent configurations reported in Fig. 4(c)–(e) are considered.

The correspondent TAC and the eco-indicator values are summarized in Table 3. It is possible to notice that all the thermodynamically equivalent configurations realized a better performance than the reference hybrid configuration. Among all the thermodynamic equivalent configurations, the one reported in Fig. 4(e) exhibits the better performances in terms of TAC, and the corresponding Pareto-optimal solutions graph is reported as Supplementary Material in Fig. S1. Anyway, the thermally coupled configuration of Fig. 3(c) remains the best alternative when both the TAC and eco-indicator are considered. This result was expected since thermodynamically equivalent configurations have the same energy consumption of the thermally coupled configurations from which are derived (Rong et al., 2004).

6.5. Intensified alternative configurations

In this section, only the intensified configurations derived from the thermodynamically equivalent alternatives discussed in the previous paragraph are considered. The comparison indexes for the alternatives reported in Fig. 5(c)–(e) are summarized in Table 3. Considering the TAC, all the intensified alternatives have a lower value compared to the reference configuration of Fig. 2. In particular, configuration of Fig. 5(e) has the lowest TAC value among all the alternatives. Compared to the best thermally coupled configuration of Fig. 3(c), it has 15% savings in the TAC with a 25% penalty in the eco-indicator. The highest value of the eco-indicator is due to the increase of the total reboiler duty in the intensified configuration and the consequent increase in the carbon dioxide emission that penalizes the environmental index. The detailed design of the configuration in Fig. 5(e) is reported in Table 6 and the Pareto-optimal solutions graph in Fig. 7. In the Pareto-front, the selected solution is marked with a circle.

7. Result extension for a typical industrial plant capacity

In this section, the reference configuration of Fig. 2, the best thermally coupled configuration of Fig. 3(c) and the best intensified configuration of Fig. 5(e) were simulated considering a feed flowrate of 61,071 kg h^{−1} according to Mariano et al. (2011). The same settings discussed in Section 5 were considered in all the simulations. The results were summarized in Table 7. It is possible to notice that the thermally coupled configuration exhibits a 41% reduction of the TAC and a 44% decrease of the eco-indicator,

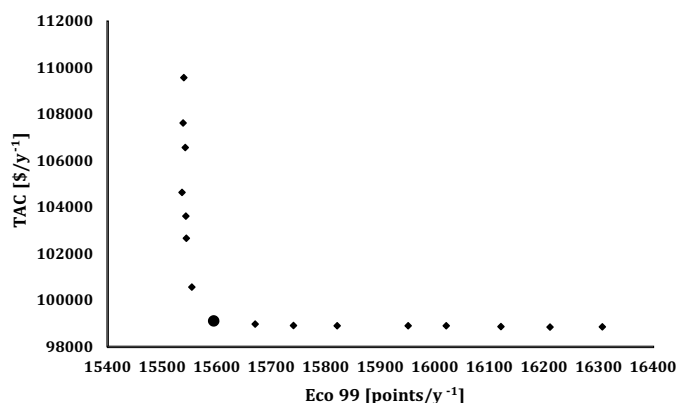


Fig. 7. Pareto-optimal solutions for the configuration of Fig. 5(e).

Table 7

Total annual cost and eco-indicator 99 for selected configurations.

Configuration	TAC (\$ y ⁻¹)	Eco-ind. (points y ⁻¹)
2	150,277,975	56,975,452
3(c)	106,754,390	39,651,947
5(e)	105,984,077	40,501,087

compared to the reference case of Fig. 2. For the intensified sequence both the indexes are lower than the reference case, but compared to the thermally coupled alternative, a 2% penalty of the eco-indicator was observed.

8. Conclusions

Butanol produced by fermentation processes represents a sustainable alternative to petro-derived fuels. The optimization of the process is a fundamental step to bring a competitive production alternative to the synthesis production path. In this context, the study of the products separation section and the generation of alternative configurations are of meaningful importance. Different alternatives are presented derived from a reference hybrid liquid–liquid and distillation flowsheet. Thermally coupled, thermodynamic equivalent and intensified configurations have been proposed. Compared to the reference, all the new alternatives have a lower TAC value. In particular, the thermally coupled configuration with two thermal couplings realizes a 24.5% saving in the TAC and 11.8% reduction of the eco-indicator compared to the reference. Moreover, among all the intensified structures, one realized a 43% reduction of the TAC, but with a penalty of 16.5% in the eco-indicator. This penalty was reduced to 2% when a higher feed flowrate was examined.

The new configurations proposed have the potential to reduce the costs associated to product recovery section for the biobutanol production also when a typical industrial capacity is considered.

The results discussed are valid for the specific feed composition case considered but should be emphasized that the generation of alternatives is a general procedure reproducible for any other feed composition.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.compchemeng.2015.10.009>.

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