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Biobutanol Purification by Liquid-Liquid Extraction Assisted Divided Wall Columns

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Biobutanol is receiving a great interest from both academia and industry sectors, and some companies are already focused on revamping bioethanol plants to produce biobutanol. The recovery of fuel grade butanol by distillation was proved to be not economically sustainable. On the other side, hybrid flowsheets, obtained combining liquid-liquid extraction and distillation, were proved to be a valid alternative. Divided wall columns, as one of the most promising intensified distillation alternatives, were here explored in combination with liquid-liquid extraction. A multiple objective function taking into account the economy, the environmental impact and the process controllability was defined to screen the alternatives. Among all the configurations considered, liquid-liquid extraction combined with a DWC equipped with two reboilers and a side rectifier, reached 22% and 18% reduction of the economy and environmental index respectively in comparison with conventional schemes. At the same time, also the controllability was improved compared to the hybrid liquid-liquid assisted simple column distillation sequence considered as a reference.

1. Introduction

The Acetone, Butanol, Ethanol (ABE) fermentation process was popular in the time window between the World War I and the developing of the petrochemical industry. Nowadays, it is now coming back into the spotlight due to the physicochemical biobutanol properties. Researching on biobutanol recovery are gaining importance in the industrial sector since different companies already started retrofit projects to convert bioethanol to biobutanol production plants. In example, BP declared that a $ 30 million retrofit investment on a $ 100 million ethanol plant could allow a facility to switch easily between producing ethanol or butanol from the same feedstock. Comparing bioethanol and biobutanol physical properties, biobutanol has a higher energy density, and a lower tendency to absorb water, moreover biobutanol/gasoline blends are less corrosive making possible the use of the existing distribution infrastructures. Nevertheless, considering 1 kg of corn as feedstock, the yield of pure bioethanol is 0.30 kg and only 0.11 kg for the biobutanol production. Distillation, as one of the most widespread separation method, was initially applied for the separation of ABE mixtures. Marlatt and Datta (1986) proposed a three-column plus two-stripper configuration. Different alternatives have been successively proposed by Kraemer et al. (2011) among the others. Nevertheless, since most of the alcohol mixtures obtained by fermentation are diluted and non-ideal, their separation by distillation is too energy intensive, penalizing the whole process economic profitability. In particular, the ABE mixture has a homogeneous azeotrope between ethanol and water and a heterogeneous azeotrope between butanol and water and the combination of different unit operations appears the most efficient way to perform the separation. Liquid-liquid extraction assisted distillation was proved to be an efficient combination for the ABE separation. In the present work the hybrid liquid-liquid extraction assisted distillation flowsheets are considered focusing on alternatives with divided wall columns (DWCs). DWCs were already proved to be an effective solution for biofuels separation. In the present work a complete set of DWCs is presented and compared

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considering a multi-objective function obtained by the combination of three different indexes to take into account the economy, the environmental impact and the controllability of the alternatives.

2. Methodology

2.1 Hybrid schemes synthesis procedure

The synthesis procedure is an essential tool used in the generation of the searching space that includes all the possible configurations to be explored. This step avoids the adaptation of known configurations to the specific case considered or any other activity that brings to the definition of an incomplete set of alternatives that eventually leads to ignore potentially optimal solutions. The number of sequences can be evaluated according to the formula reported by Thompson and King (1972). Following this methodology, liquid-liquid extraction assisted simple distillation columns, are considered first. In these hybrid flowsheets the solvent phase is fed to the distillation section. For the ABE separation case, this stream is expected to be a 4-component mixture containing the solvent, the acetone, the butanol and ethanol; then 5 simple column sequences are possible. Starting from a liquid-liquid assisted simple column configuration, it is possible to substitute in a combinatorial way, two of the three columns with a ternary conventional DWC. Two possible alternatives are reported in Figure 1; the hybrid liquid-liquid extraction indirect simple column configuration (HLL-ISC) and the hybrid liquid-liquid extraction indirect-direct simple column configuration (HLL-IDSC). Considering the HLL-ISC reported in Figure 1(a), the resulting configurations are reported in Figure 2. The conventional DWC substitutes always two columns, the resulting hybrid flowsheet is then composed by a sequence of the liquid-liquid extractor, a simple column and the DWC.

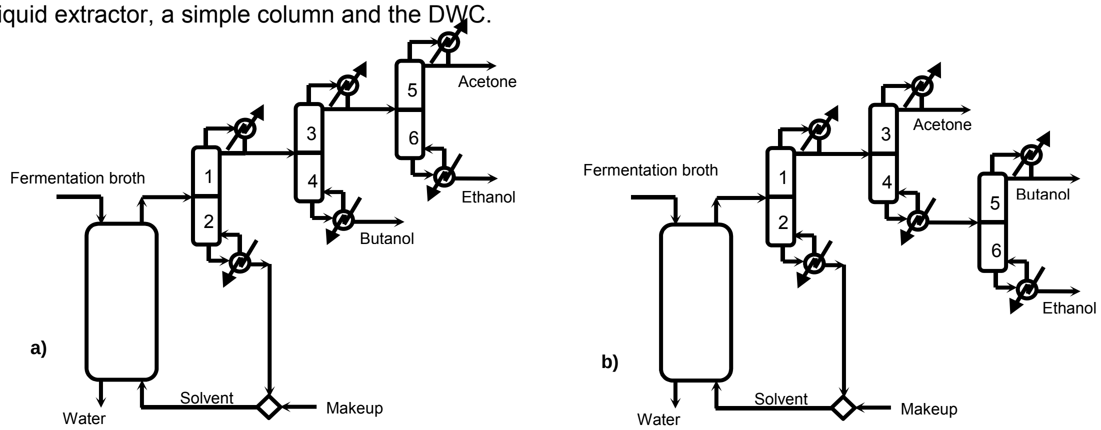

Figure 1 Liquid-liquid extraction assisted simple columns: (a) indirect sequence (HLL-ISC), (b) indirect-direct sequence (HLL-IDSC)

Differently from the case of conventional DWCs, to generate non-conventional DWCs it is required a more structured systematic synthesis methodology. A non-conventional DWC is here defined as a column that could include multiple reboilers/condensers and/or intermediate reboilers and multiple walls.

The synthesis procedure can be explained as follow Rong (2011).In the first step, a simple column configuration is selected from the subspace including all the possibilities. In the second step, the original thermally coupled configurations are considered. These are obtained from the simple column configurations by elimination, in a combinatorial way, condensers and/or reboilers associated to non-product streams. Those exchangers are replaced by bidirectional thermally coupled vapor and liquid streams. This step is accomplished by substitution of the first column condenser. The third step regards the generation of the thermodynamic equivalent structures from the corresponding original thermally coupled configuration by rearranging the column sections connected by thermal couplings. This step brings to a configuration with a side stripper connecting the two remaining columns. In the last step, the multicomponent DWCs are obtained from the thermodynamically equivalent configurations by incorporating the single column section into its thermally linked column through a dividing-wall. In the example considered the stripper section is implemented inside the column. As a result, the DWC with two reboilers is obtained. All the possibilities obtained from the HLL-ISC are summarized in Figure 3.

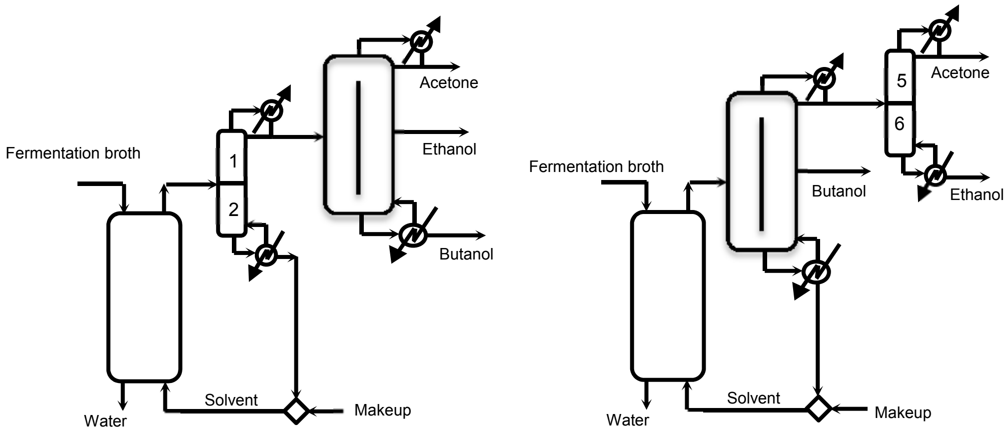

Figure 2. Liquid-liquid extraction assisted conventional DWC configurations

In order to compare the different hybrid flowsheets, a feed of 1.64 kmol h-1 composed, in molar bases, by 8.1% acetone, 11.3% butanol, 0.4% ethanol and 80.2% water at 35°C and 1 atm, was considered. The composition was defined according to Wu et al. (2007). All the proposed configuration have been simulated using Aspen Plus V8.8. The NRTL-Hayden O´Connell equation of state with Henry´s law was selected as thermodynamic model and hexyl-acetate was used as a mass separation agent. The minimum purity targets were fixed on mass base to 99.5% for acetone and biobutanol, and 99.0% for ethanol.

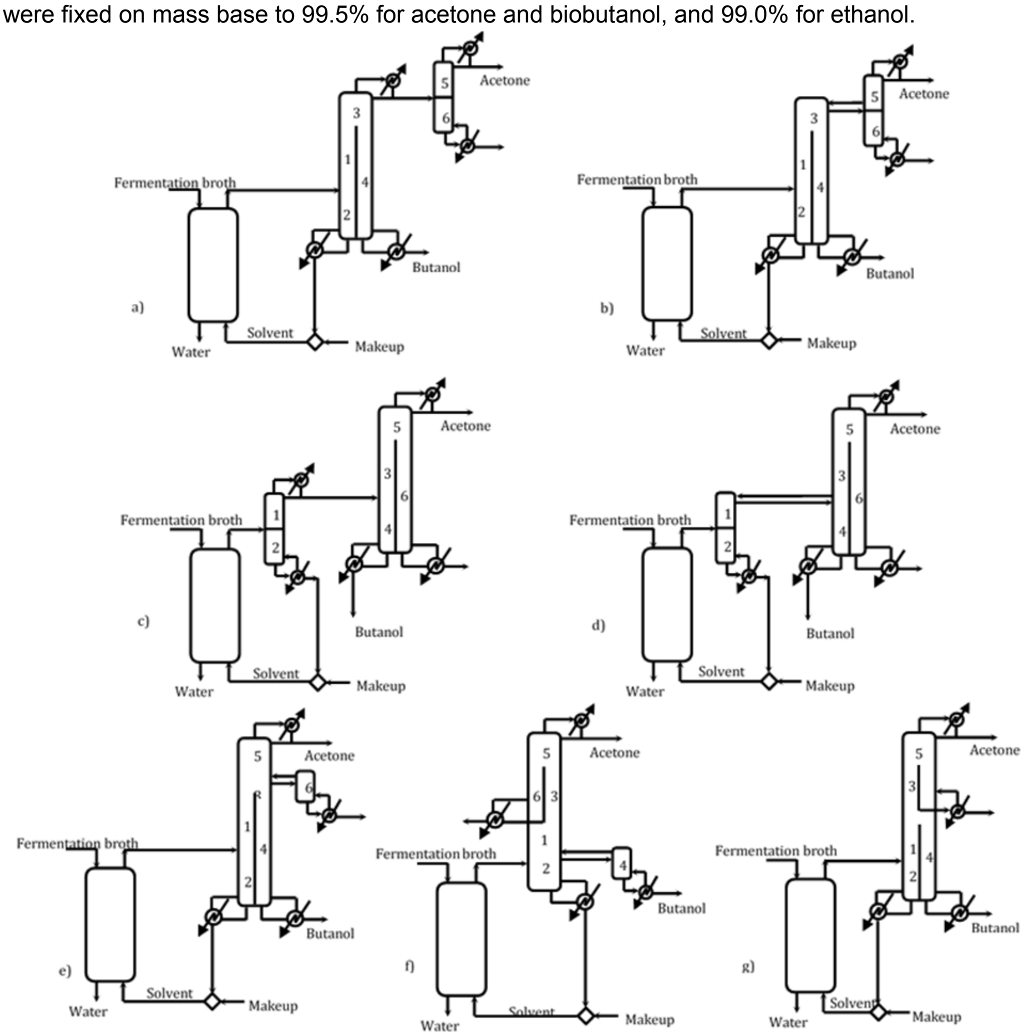

Figure 3. Liquid-liquid extraction assisted non-conventional DWC configurations

2.2 Optimization Procedure

The design of the different alternatives proposed was performed minimizing the multi-objective function reported in Eq. 1:

$$Min(TAC, EI99, CN) = f(N_e, N, N_f, RR, D, F_L, F_V, \phi, S) \quad (1)$$

Subject to $\vec{y} \geq \vec{x}$

Where TAC is the total annual cost, EI99 is the eco indicator 99, CN is the condition number, N_e is the number of stages for the extractor, N is number of stages for the distillation columns, N_f is the column feed stage, RR is the reflux ratio, D is the distillate flow rate, F_L is the interconnection liquid flow rate, F_V is the interconnection vapor flow rate, ϕ is the column diameter, S is the solvent flow rate; y and x are the vectors of obtained and required purities, respectively. Due to the complexity of the problem, Differential Evolution with Tabu List (DETL) was used as optimization algorithm. Differential evolution algorithm is based on 4 main steps: initialization, mutation, crossover and selection. In order to implement the optimization algorithm, Aspen Plus was linked to Microsoft Excel and Matlab using the dynamic data exchange by COM technology.

2.3 Objective functions

The design of the hybrid liquid-liquid extraction assisted distillation flowsheets was performed by minimizing an object function composed by the total annualized cost, the eco-indicator 99 and the condition number.
The total annualized cost is the index used in the objective function to take into account the economy of the process. It is evaluated as the sum of the annualized capital cost and the operating costs as reported in the Eq. 2:

$$TAC = \frac{Capital\ costs}{Project\ life} + Operating\ Costs \quad (2)$$

The capital costs include the cost of the columns (shell and trays), kettle reboilers and shell and tube condensers. The capital cost was annualized considering a project life equal to 10 years.

The Eco Indicator 99 (EI99) was used to quantify the environmental load of the flowsheets over the life cycle. In the EI99 methodology, 11 impact categories are considered aggregated into three major damages categories: human health, ecosystem quality, and resources depletion.
It was quantified following the procedure proposed by Goedkoop and Spriensma (2001) as reported in Eq. 3:

$$EI99 = \sum_b \sum_d \sum_{k \in K} \delta_d \omega_d \beta_b \alpha_{b,k} \quad (3)$$

Where βb 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. The scale is chosen in such a way that the value of 1 Pt is representative for one thousandth of the yearly environmental load of one average European inhabitant. In this work, for eco-indicator 99 calculation the impact of three factors were considered as most important in the ABE downstream processing: steam (used in column reboiler), electricity (used for pumping) and steel (to build distillation columns and accessories).The values for those three factors are summarized in the manual reported by Goedkoop and Sprinsma (2001), also are shown in Table 1.
The condition number (CN) is used as index to evaluate the controllability properties defined in Eq. 4, is the ratio between the largest and the smallest singular values and is used to qualitatively measure the sensitivity to uncertainty. In terms of controllability, a large condition number indicates that it will be inconvenient to satisfy the entire set of control objectives (notwithstanding the control strategy to be used). Physically the condition number represents the ratio of the maximum and minimum open-loop, decoupled gains of the system. A large condition number suggests that the relative sensitivity of a system in one multivariable direction is very poor. In general, configurations with a high minimum singular value and low CN are expected to have best dynamic performances under feedback control.

$$CN = \frac{\sigma_{max}}{\sigma_{min}} \quad (4)$$

For each process design is possible to generate a relative gain matrix in the nominal state, the correspondent CN is obtained in an open-loop control policy. The elements of each matrix are calculated considering a 0.5% positive disturbance in the nominal state of manipulated variable value (reflux ratio, reboiler heat duty, side stream flowrate and so on). The impact of the perturbations is low enough to assume a first order response. The SVD method, and consequently the singular values, depends on the scaling of the input and outputs. To remove this dependency different scaling methods have been proposed. For the configurations reported in this study control variables like the products purity there are naturally bounded between 0 and 1, but the reflux ratio, and in general all the streams flowrate are unbounded. Note that, since Condition Number is a qualitative control measurement, the different values produced of condition number do not indicate that a scheme is any times better than other, the difference in condition number values only means that a scheme is better than other regarding to control properties.

Table 1. Unit eco-indicator used to measure the eco-indicator 99 in both case studies

Impact category	Steel (points/kg)	Steam (points/kg)	Electricity (points/kWh)
Carcinogenics	6.320E-03	1.180E-04	4.360E-04
Climate change	1.310E-02	1.600E-03	3.610E-06
Ionising radiation	4.510E-04	1.130E-03	8.240E-04
Ozone depletion	4.550E-06	2.100E-06	1.210E-04
Respiratory effects	8.010E-02	7.870E-07	1.350E-06
Acidification	2.710E-03	1.210E-02	2.810E-04
Ecotoxicity	7.450E-02	2.800E-03	1.670E-04
Land Occupation	3.730E-03	8.580E-05	4.680E-04
Fossil fuels	5.930E-02	1.250E-02	1.200E-03
Mineral extraction	7.420E-02	8.820E-06	5.7EE-6

3. Results

Comparing the results reported in Table 2, it is possible to notice that, from an economic point of view, all the liquid-liquid assisted DWCs have a lower value of the TAC respect to the best liquid-liquid assisted simple column distillation reported in Figure 1(a). Among the liquid-liquid assisted conventional DWCs, the configuration of Figure 2(a) showed the lowest values of all the objective functions. If compared to HLL-ISC configuration, it realized 13.6% reduction of the TAC and a better controllability, nevertheless a penalty of 12.5% in EI99 is observed. The penalty is due to the highest DWC utility consumption. When the solvent is recovered as bottom stream in the DWC, as depicted in Figure 2(b), the TAC and the EI99 resulted penalized compared to the reference case of Figure 1(a). Considering the liquid-liquid assisted non-conventional DWCs, the configuration of Figure 3(g) has the lowest TAC and EI99 but is penalized by its controllability. The economic performance of the configuration of Figure 3(g) were expected since is the more intensified alternative where the solvent and the ABE mixture were separated in the same column. Extending the comparison to the best liquid-liquid assisted simple column distillation, the configuration of Figure 3(e) realized better performance for all three objective functions. In particular reached 22% and 18% reduction of the TAC and EI99 respectively, together with a better controllability index. Details on the configuration of Figure 4(e) are reported in Table 3. From the structural point of view, configurations 4(e) and 4(g) differ only for column section 6. In the configuration of Figure 3(e) there is a single rectifying section whereas in Figure 3(g) this section is implemented in the DWC. The differences between the two configurations regarding the TAC and the EI99 are lower than 5%, nevertheless the highest value of the CN for the configuration of Figure 3(g) brings to the conclusion that the alternative 4(e) is the absolute best one. Other two configurations exhibited interesting performance; Figures 3(b) and (d) have lower values of the objective functions than the reference case, and the difference respect to the best alternative is lower than 5%. These configurations belongs to the group where the DWC is thermally coupled with the simple column. So, in the continuous search to find better values for condition number, some other energetic or economic indexes are sacrificed and vice versa. Highly intensified systems (aiming at minimizing energy consumption under specific designs) imply a high degree of nonlinearity and interaction between variables, and loss of control degrees of freedom that restrict the operating conditions flexibility of the system, so the feasibility to find a good dynamic behavior zone it depends totally of a correct addressing as concern to energy consumption.

Table 2: Objective function values for the configurations of Figure 3

Objective Function	Fig 4(a)	Fig 4(b)	Fig 4(c)	Fig 4(d)	Fig 4(e)	Fig 4(f)	Fig 4(g)
TAC [k$ yr-1]	108.54	105.57	115.50	101.78	100.85	100.59	97.88
EI99 [kpoints yr-1]	13.73	12.93	14.34	13.30	12.79	14.74	12.22
CN	1402	1.7	$1.22 \cdot 10^{17}$	3.9	7.3	9888.3	18994.4

Table 3: Design and Operative Parameters for the Configurations in Figure 4(e)

4 e		Column	Section			**1b)**			
	Extractor	1+2	4	5+3	6	Extractor	C1	C2	C3
Number of stages	5	43	43	71	7	5	23	47	46
Feed location	---	13	---	---	---		12	31	14
Distillate flowrate [kg h-1]	---		---	0.644	---		21.685	7.706	0.331
Liquid split flowrate [kg h-1]	---	---	---	7.717	---				
Vapor split flowrate [kg h-1]	---	43.463	17.383	---	---				
Extract flowrate [kg h-1]	---	---	---	---	---				
Solvent flowrate [kg h-1]	733.873	---	---	---	---	733.873			
Reboiler duty [kW]	---	69.92	0.633	0	0.023		66.222	8.256	0.883
TAC [k$ yr-1]			100.85					134.79	
EI99 [kpoints yr-1]			12.79					13.93	
CN			7.3					616636.85	

4. Conclusions

Biobutanol, as potential bioethanol competitor, is reaching the industrial interest; despite its production process is far away to be optimal. Improvements in the separation of biobutanol, acetone and ethanol by hybrid liquid-liquid assisted distillation were considered. In particular new hybrid arrangements composed by liquid-liquid extraction and different divided wall configurations were systematically generated. All the alternatives were optimized using a triple objective function composed by the total annual cost, the eco indicator 99 and the condition number. The multi-objective function takes into account the economic, the environmental and the controllability behavior. The alternatives were compared to the liquid-liquid assisted simple column distillation. In the best configuration selected, the extract stream is fed to a DWC equipped with two reboilers and a side rectifying stream. For this configuration a reduction of 22% of the TAC and 18% of EI99 was observed together with a better condition number. Other two configurations reached promising performance with less than 5% difference compared to the best alternative and a better controllability. The configurations proposed have been never considered for the ABE separation and they represent a concrete possibility to improve the biobutanol process competitiveness.

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