SEPARATION OF ACETONE-BUTANOL-ETHANOL MIXTURE BY A HYBRID PROCESS

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Biobutanol is considered an alternative biofuel which can be obtained through acetone-butanol-ethanol (ABE) fermentation process with low concentration (<3%wt.). The aim of this work is to design an energy-efficient hybrid separation system by combining distillation with liquid-liquid extraction. In this way, the most plentiful component (water) can be removed with minimum costs. Two hybrid separation sequences are designed (one uses mesitylene and the other 2-ethyl-1-hexanol as separation agent), optimized and economically evaluated. The total annual cost and the energy requirements are reduced with 25% and 34% respectively by using dividing wall column and heat integration.

Keywords: Downstream processing, liquid-liquid extraction, distillation, dividing-wall column, heat integration

1. Introduction

The increase of global energy demand and the importance of environmental safety are two important aspects that lead nowadays to a possible depletion and price rise of fossil fuels. Therefore, biofuels are environmentally friendly and significantly reduces the gas emissions. Biobutanol is considered a bio-derived fuel with high energy content (32 MJ/kg butanol) that can be produced in the acetone-butanol-ethanol (ABE) fermentation process. Lately, biobutanol gained interest over ethanol thanks to its characteristics as low water miscibility, low flammability and corrosivity, and being able to replace gasoline in car engines [1]. Biobutanol can be produced on an industrial scale from lignocellulosic feedstocks like corn stover, wheat straw, corn fiber, barley straw, switchgrass or wood residue [2]. The best butanol concentration was obtained using microorganisms such as Clostridium Acetobutylicum and Clostridium Beijerinckii. However, through the fermentation process, butanol cannot exceed 3% wt. in broth, because butanol inhibits the activity of microorganisms [3]. The fermentation process requires genetic engineering to increase the concentration of

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butanol, which will reduce the energy demand in downstream processing and will provide an economical process of ABE separation [4].

The separation of diluted ABE mixture can be achieved through different separation technics: distillation, liquid-liquid extraction, adsorption, gas extraction, reverse osmosis, perstraction, flash vacuum pervaporation and hybrid separation [1]. Distillation is a separation technique largely used in industry, with high potential of process intensification and heat integration. The separation of ABE mixture by distillation is an energy intensive method (14.7 to 79.05 MJ/kg butanol) [1]. However, a new separation sequence was published, where the energy requirement was reduced to only 2.7 MJ/kg butanol by using vapor recompression (VRC) and heat integration in an azeotropic dividing-wall column (A-DWC) [5,6].

This work presents two hybrid separation sequences which combine liquid-liquid extraction with conventional distillation columns. The liquid-liquid extraction is performed with two different solvents (mesitylene and 2-ethyl-1-hexanol). Both separation sequences are designed and optimized for a minimum total annual cost (TAC). The most efficient hybrid sequence is further subject to process intensification through dividing-wall column technology and heat integration. Therefore, a new hybrid separation process is designed which features 34% energy and 25% TAC savings compared to the conventional hybrid separation sequence.

2. Problem statement

The ABE mixture obtained from the fermentation process contains a large amount of water. Separation of water by distillation requires a large amount of energy. The liquid-liquid extraction technique can solve this problem by eliminating the most plentiful component (water) without energy costs. This technique requires a good solvent with low viscosity, different density than water, high selectivity for butanol and which does not form azeotropes with the components from the mixture [4, 7]. There are several solvents used for ABE recovery e.g. oleyl alcohol, n-hexyl acetate, mesitylene and 2-ethyl-1-hexanol [4, 7, 8, 9]. The most energy-efficient hybrid processes are obtained using mesitylene (4.8 MJ/kg butanol) and 2-ethyl-1-hexanol (9.37 MJ/kg butanol) [4, 9]. However, these two studies neglect the impurities (acetic acid and butyric acid) present in the ABE mixture. According to azeotropic data predicted by Aspen Plus, mesitylene forms a high boiling point azeotrope with butyric acid (Table 1). Moreover, this azeotrope can accumulate in the solvent recycle and must be removed, leading to a high economic penalty. This work considers a feed stream mixture of 4.5%wt. acetone, 18.6%wt. butanol, 0.9 %wt. ethanol, 75.9 %wt. water and ppm butyric acid and acetic acid, which can be recovered from fermentation

by gas stripping [8]. The constraints of downstream processing are a production rate of 40 kt/years butanol at 99.4 %wt. purity and water removal at 99.8 %wt.. Both mesitylene and 2-ethyl-1-hexanol are considered as potential solvents.

Two hybrid processes with conventional distillation columns are compared hereafter, in terms of energy requirement and total annual cost. The best hybrid separation sequence is further studied for total annual cost reduction by using dividing-wall column technology and energy minimization by heat integration.

Table 1

Azeotropes

Temp (°C)	Type	Acetone	Butanol	Ethanol	Acetic Acid	Butyric Acid	Water	Mesitylene	2-Ethyl-1-Hexanol
95.91	Heterogeneous	-	0.42	-	-	-	0.58	-	-
93.97	Heterogeneous	-	0.25	-	-	-	0.42	0.33	-
78.15	Homogeneous	-	-	0.96	-	-	0.04	-	-
99.18	Homogeneous	-	-	-	0.36	-	0.64	-	-
96.05	Heterogeneous	-	-	-	0.20	-	0.42	0.38	-
99.82	Homogeneous	-	-	-	-	0.15	0.85	-	-
96.61	Heterogeneous	-	-	-	-	0.01	0.53	0.46	-
154.62	Homogeneous	-	-	-	-	0.37	-	0.63	-
96.61	Heterogeneous	-	-	-	-	-	0.53	0.47	-
99.34	Heterogeneous	-	-	-	-	-	0.85	-	0.15

3. Modeling approach

The design and optimization of each separation sequence is performed with Aspen Plus simulation software using NRTL property method to model the non-ideality of the liquid phase. The binary parameters between butyric acids and solvents are estimated by UNIFAC method. Fig. 1 shows that mesitylene forms an azeotrope with butyric acid (left), meanwhile 2-ethyl-1-hexanol does not (right).

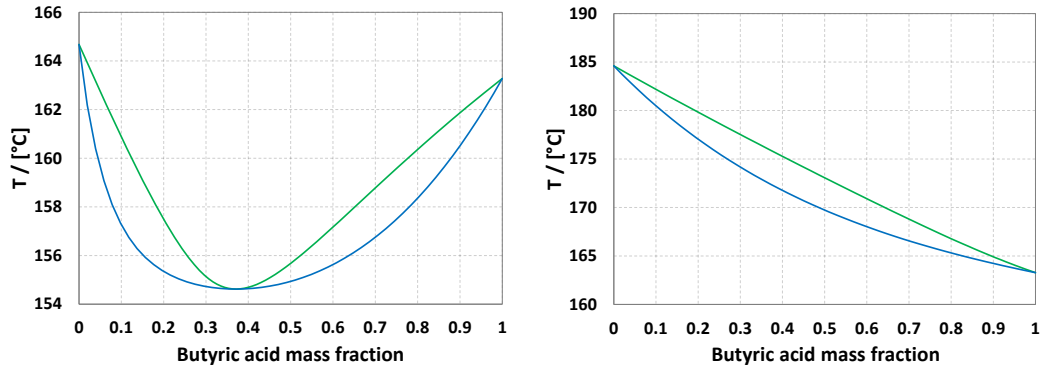

Fig. 1. T-xy diagram for solvent - butyric acid (mesitylene – left, 2-ethyl-1-hexanol – right)

The conceptual design is based on the following approach:

- remove the most plentiful component (water) by liquid-liquid extraction;

- recover the solvent with high purity;
- perform last the most difficult separation (butanol purification);
- purify the water product by removing the light components (acetone, ethanol)

The liquid-liquid extraction column is designed for counter current flow. The minimum solvent flow rate is found by using equations (1) – (2), where X_E, X_S, X_F and X_R represent the molar fraction of butanol in the extract, solvent, feed and raffinate, respectively; E, S, F and R are the molar flow rates of the same streams.

$$\frac{R}{S} = \frac{X_E - X_S}{X_F - X_R}, \tag{1}$$

$$X_E \cdot E = X_F \cdot F + X_S \cdot S - X_R \cdot R, \tag{2}$$

$$N = \frac{\log\left[\left(\frac{\varepsilon - 1}{\varepsilon}\right) \cdot \left(\frac{X_F - X_S / K}{X_R - X_S / K}\right) + \frac{1}{\varepsilon}\right]}{\log \varepsilon}, \tag{3}$$

The molar fractions of the butanol in the raffinate and extract are obtained from the liquid – liquid equilibrium diagrams (Fig. 2) calculated by the Aspen Plus simulator, using the NRTL property model. The mass balance of the extraction column can be calculated using the equation (2). The theoretical number of stages is given by the equation (3), where K is the slope of the equilibrium line and ε is the extraction factor. Due to different selectivities of the solvents for butanol, a minimum of 14525.5 kg/h mesitylene or 1273.7 kg/h 2-ethyl-1-hexanol are required for liquid-liquid extraction.

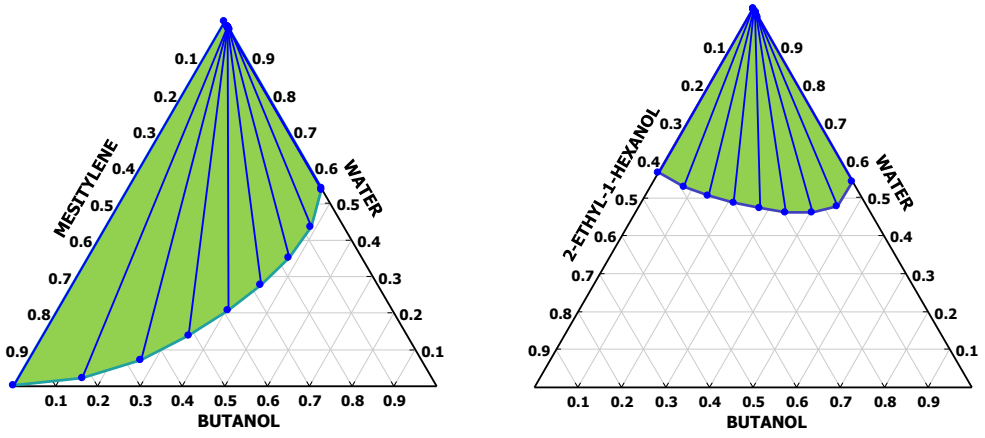

Fig. 2. Liquid – liquid equilibrium line of the butanol – water – solvent

4. Process design

4.1. Design of the process using mesitylene as extraction solvent

The diluted ABE mixture and the solvent are fed on the top tray and on the bottom tray of the liquid-liquid extraction column, respectively. The raffinate containing water, acetone and ethanol is further sent for purification in the distillation column COL-3. The extract contains mainly solvent, butanol, acetone and ethanol. However, the liquid-liquid extraction selectivity in not 100%, and a small amount of water remains in the extract. The first distillation column (COL-1) serves to solvent recovery. Due to the presence of the butyric acid - mesitylene azeotrope, a side stream is necessary to avoid the accumulation of acids in the solvent recycle stream. The second distillation column (COL-2) separates the butanol in bottom and acetone - ethanol as distillate. A side stream is also required for COL-2 to recycle a small amount of butanol-water azeotrope. In the third column (COL-3), the distillate of the COL-2 and the raffinate are fed together for water purification. The side stream of COL-1 is fed in the fourth column (COL-4) to avoid solvent loss. The distillation columns are optimized for a minimum of total annual cost, as it will be described in a later section. Fig. 3 presents the mass balance and key design parameters and Fig. 4 shows the composition profiles of the distillation columns.

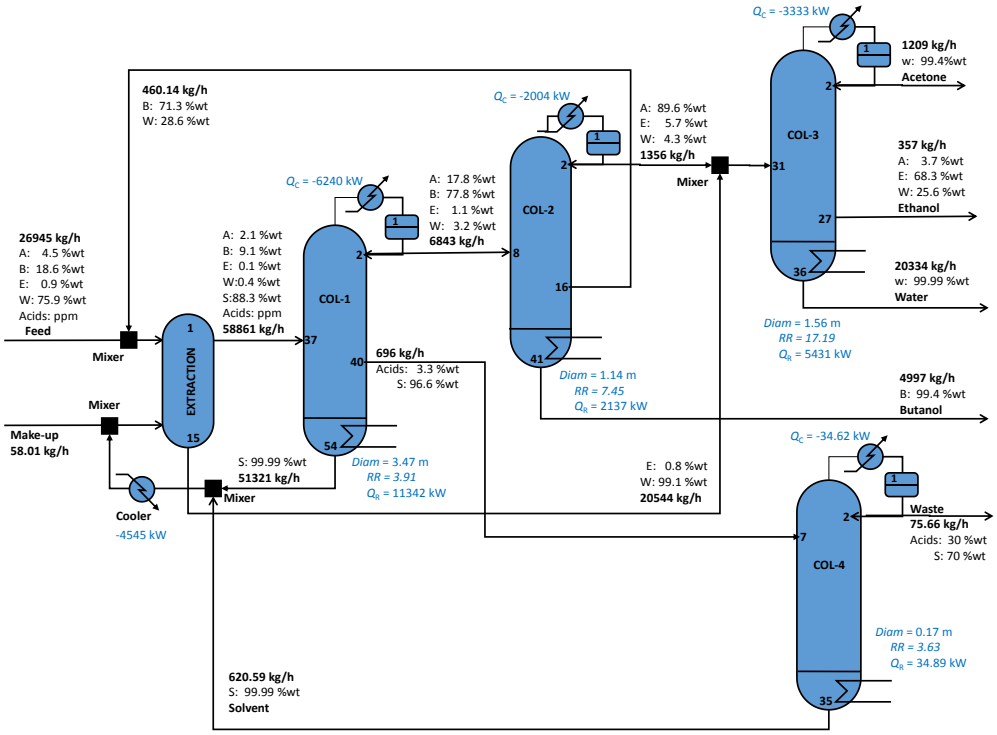

Fig. 3. Separation sequence with mesitylene as solvent

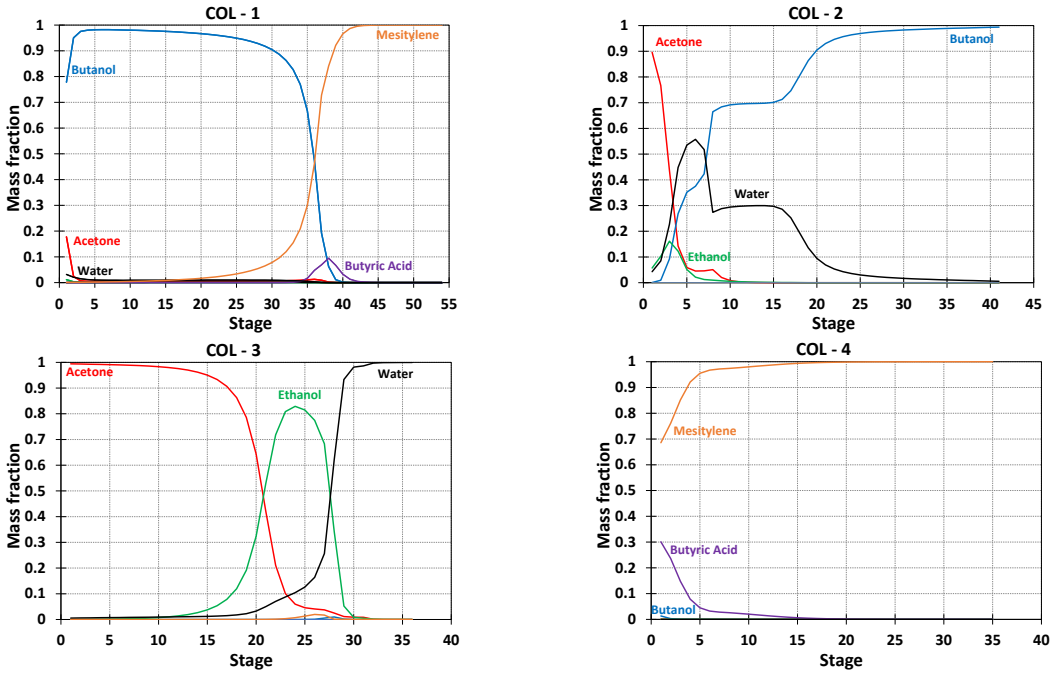

Fig. 4. Composition profiles of the distillation columns (mesitylene)

4.2. Design of the process using 2-ethyl-1-hexanol as extraction solvent

The separation sequence showed in Fig. 5 carries out the liquid-liquid extraction using 2-ethyl-1-hexanol as solvent. The ABE mixture is fed in the liquid-liquid extraction column on the top tray and 2-ethyl-1-hexanol is fed on the bottom tray. The raffinate (water with some ethanol and acetone) is sent to the column COL-3 for water purification. Because the liquid-liquid extraction process does not achieve 100% selectivity, a small amount of water is found in the extract.

The extract is fed to the distillation column (COL-1). The solvent is recovered with high purity as bottom product and recycled. The distillate is fed to the column COL-2, which delivers high-purity butanol as bottom product, acetone and ethanol with small amounts of water as distillate, and a side stream containing butanol and water. The distillate of COL-2 is sent to COL-3 for water purification. The side stream is sent to a decanter, from which the aqueous phase is recycled to the extraction column and the organic phase is fed to a lower tray of COL-2.

The distillation columns are optimized for a minimum of total annual cost, as it will be described in a later section. The mass balance and key design parameters are presented in Fig. 5. The composition profiles of distillation columns are shown in Fig. 6.

Note that this process (Fig. 5) is more promising: it does not involve the formation of an azeotrope containing the solvent, thus fewer columns are required

compared to the previous process (Fig. 3). For this reason, in the next section the energy minimization and total annual cost reduction by process intensification and heat integration will be studied.

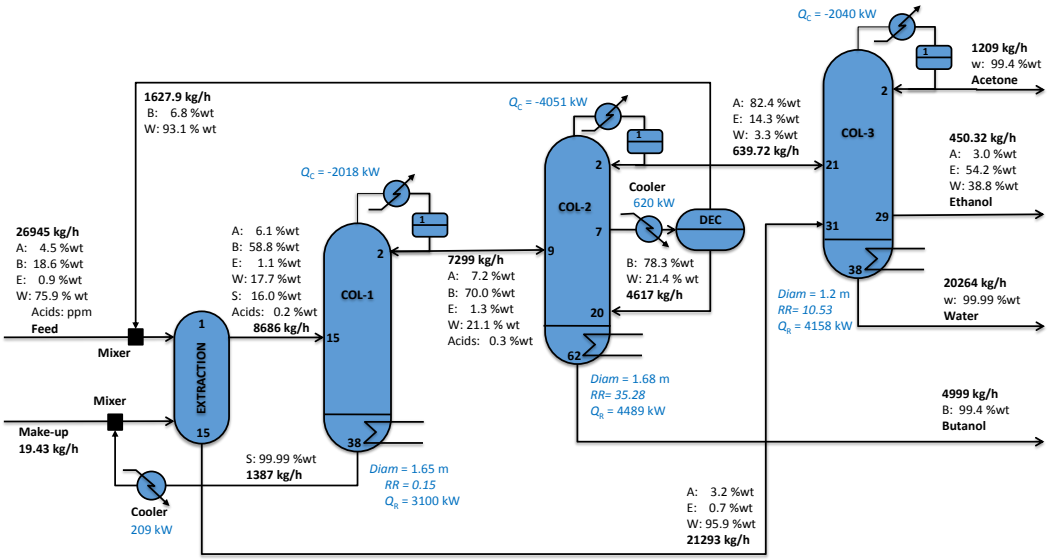

Fig. 5. Separation sequence with 2-ethyl-1-hexanol as solvent

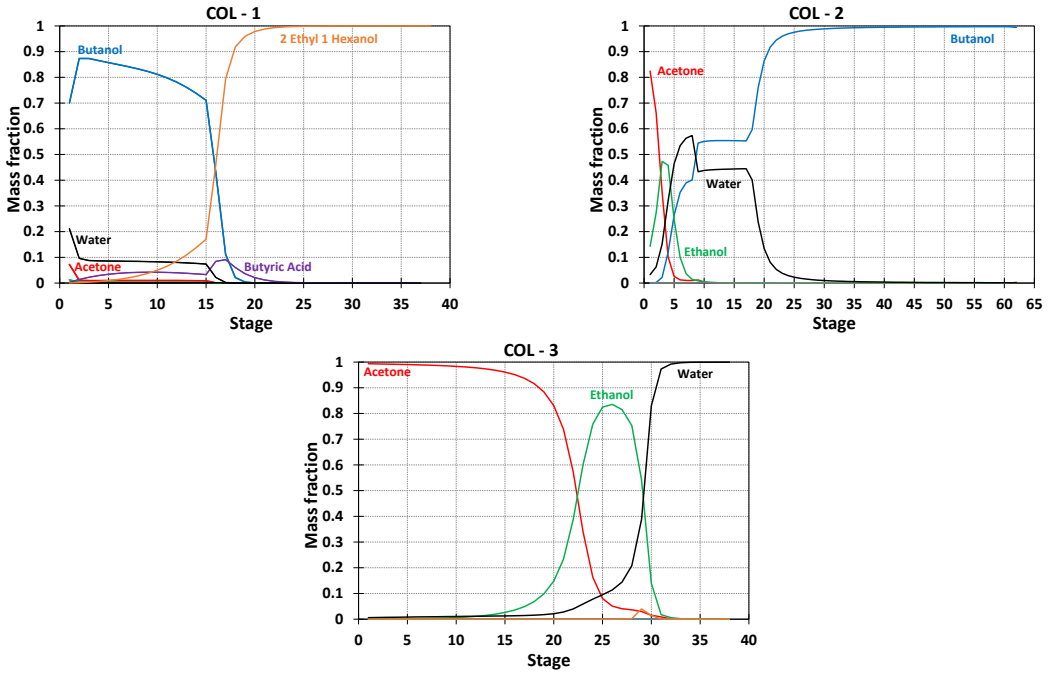

Fig. 6. Composition profiles of the distillation columns from Fig. 5 (2-ethyl-1-hexanol)

4.3. Process design alternative (2-ethyl-1-hexanol as extraction solvent)

In this section we propose a novel design alternative of separation sequence described in Fig. 5. The novel sequence uses the same extraction solvent, 2-ethyl-1-hexanol. The process flowsheet is presented in Fig. 7. This design uses a single dividing-wall (DWC) column to integrate the solvent recovery column (COL-1) and butanol purification column (COL-2). As in the previous flowsheet (Fig. 5), a butanol-water mixture is withdrawn as side stream and submitted to liquid-liquid separation (DEC), from which the organic phase is returned to DWC and the aqueous phase is recycled to extraction. Another side-stream recovers the high-butanol butanol (99.4 %wt.). The dividing-wall column is simulated in Aspen Plus as a prefractionator (PF) and a main column (DWC). The prefractionator has 30 theoretical stages and the main column has 45 theoretical stages. Note that the purpose of the column COL-3 (Fig. 5) is mainly to purify the water. For a fair assessment of energy requirements (MJ/kg butanol), the purification of acetone and ethanol should not be included in the analysis. Therefore, the column COL-3 from the conventional hybrid separation sequence (Fig. 5) is replaced by the two-product column (DC) which delivers high-purity (99.8 %wt.) water as bottoms, and an acetone-ethanol mixture impurified with small amounts of water as distillate.

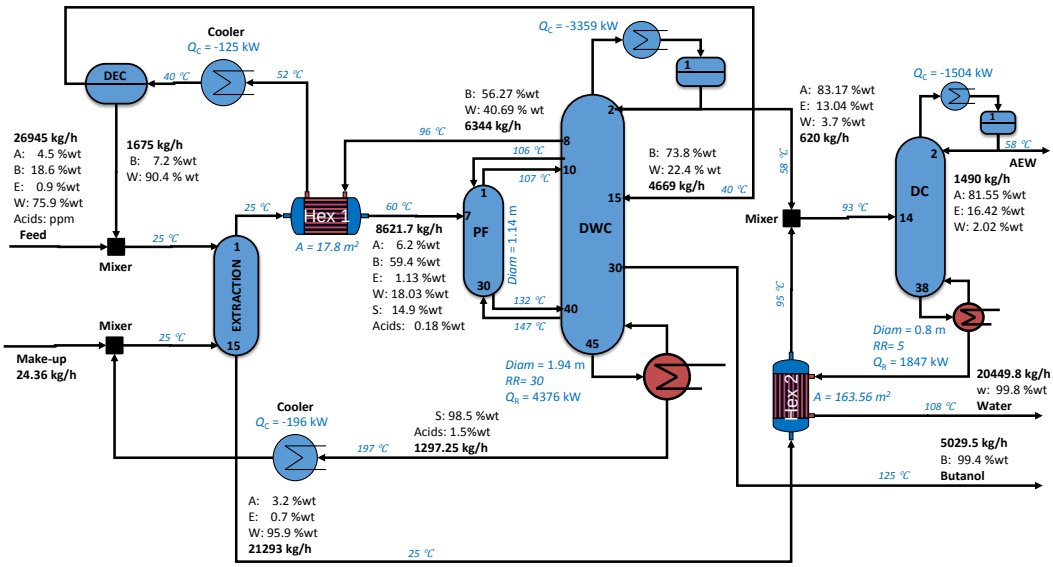

Fig. 7. Heat integrated DWC flowsheet with 2-ethyl-1-hexanol as solvent

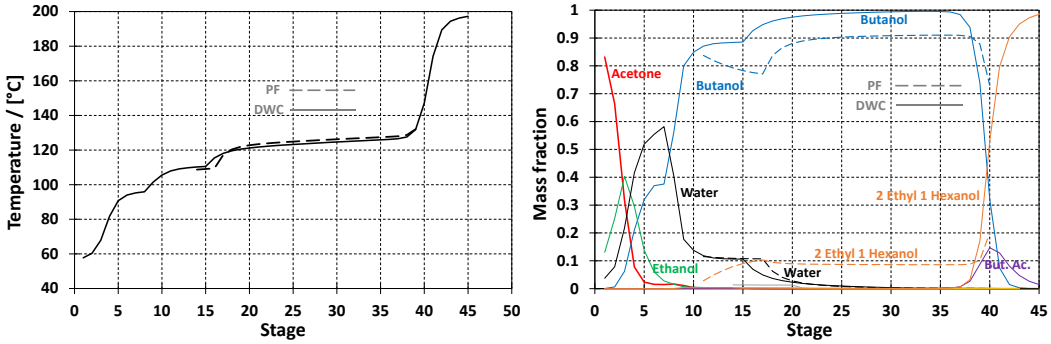

Fig. 8. Temperature and composition profile heat integrated DWC (2-ethyl-1-hexanol)

In this design, heat integration is applied for minimization of the energy requirement. Therefore, the extract is preheated to 60º before being fed to the prefractionator (PF), using the DWC side stream. The raffinate is also preheated from 25º to 95º using DC bottom stream, before being mixed with the DWC distillate and fed to the DC column. The heat integration scheme reduces the heating needs by 34%.

Fig. 7 shows the mass balance of the main streams together with the key design parameters. Fig. 8 shows the temperature (left) and composition (right) profiles of the DWC. The temperature difference between the two sides of the dividing-wall column does not exceed 20º, as required by this technology. The total annual cost is reduced by 25% compared to the conventional separation system.

5. Process optimization

In both conventional separation sequences, the distillation columns are optimized for a minimum of total annual cost (TAC).

$$TAC = OPEX + \frac{CAPEX}{payback.period}, \tag{4}$$

The equipment (CAPEX) and operating (OPEX) costs were evaluated for a payback period of 3 years and 8000 h/year operating time [10,11]. The heating utilities used are: for the solvent recovery columns (COL-1) - HP steam (42 bar, 254 °C, 9.88 $/GJ), for the butanol purification column (COL-2) and the water purification column (COL-3) - LP steam (6 bar, 160 °C, 7.78 $/GJ). The cost of cooling is $0.72/GJ. The total investment cost (CAPEX) includes the extraction column, the cooler for solvent, the distillation columns, and the decanter. The cost of the equipment was estimated using standard cost correlations (Marshall & Swift equipment cost index *M&S* = 1536.5 in 2012):

$$C_{HEX}\,(US\$) = \left(M\,\&\,S/280\right)\cdot\left(474.7\cdot A^{0.65}\right)\left(2.29+F_m\left(F_d+F_p\right)\right) \tag{5}$$

$$C_{shell}\,(US\$) = \left(M\,\&\,S/280\right)\cdot\left(957.9\cdot D^{1.066}\cdot H^{0.82}\right)\cdot\left(2.18+F_c\right) \tag{6}$$

$$C_{trays}\,(US\$) = N_T\cdot\left(M\,\&\,S/280\right)\cdot 97.2\cdot D^{1.55}\cdot\left(F_t+F_m\right) \tag{7}$$

where A is the area (m^2), F_m = 1 (carbon steel), F_t = 0 (sieve trays), F_d = 0.8 (fixed-tube), F_p = 0 (less than 20 bar), F_d = 1.35 (for reboilers), and for the shell $F_c = F_m \cdot F_p$, $F_p = 1 + 0.0074\cdot(P-3.48) + 0.00023\cdot(P-3.48)^2$.

The optimization procedure for the distillation columns followed the next steps: specify the number of stages; set design specifications in order to satisfy the constraints of product purities; perform a sensitivity analysis (included in the Aspen Plus software) to find the feed stage with the lowest energy requirement; calculate the total annual cost. Fig. 9 and Fig. 10 present the total annual cost (TAC) versus the number of stages, from which the optimum number of stages is found, for each distillation column.

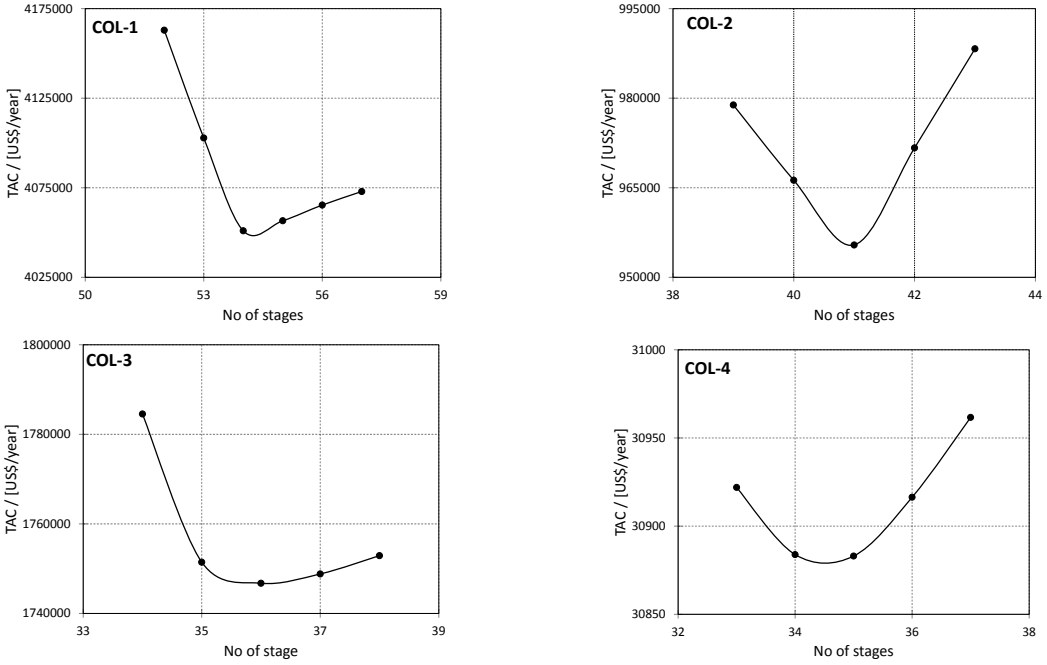

Fig. 9. Optimization of distillation columns from Fig. 3 (mesitylene)

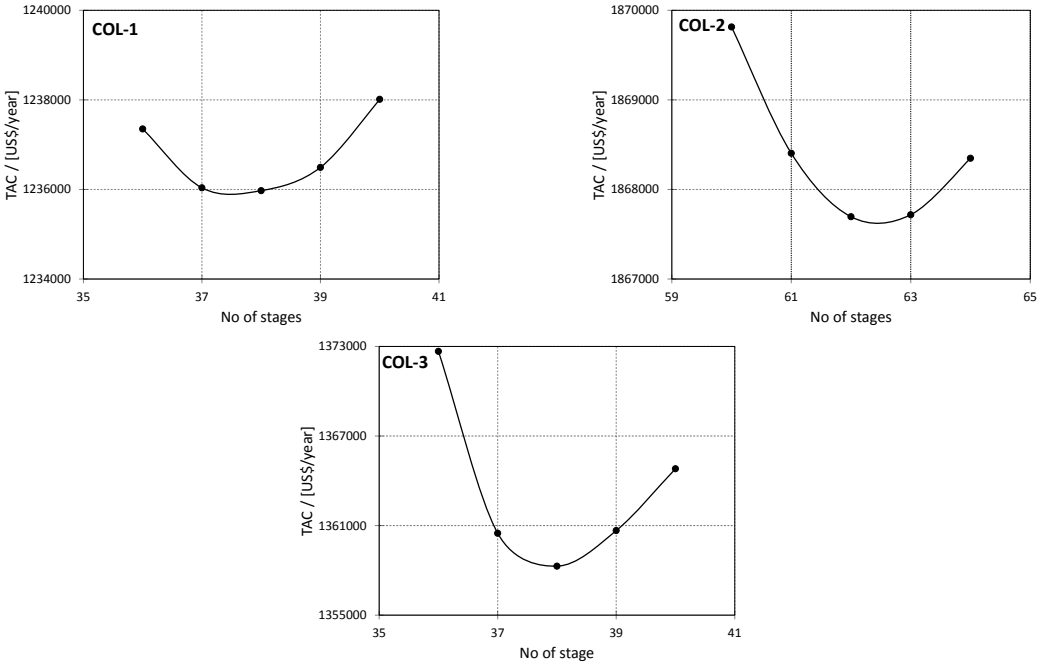

Fig. 10. Optimization of distillation columns from Fig. 5 (2-ethyl-1-hexanol)

6. Economic evaluation

Table 2 shows the economic evaluation of the separation sequence which uses mesitylene as solvent. The operating cost (OPEX) of this process is $5230 \cdot 10^3$ US$/year and the capital cost (CAPEX) is $6905.81 \cdot 10^3$ US$, which gives a total annual cost of $6890.6 \cdot 10^3$ US$/year. The energy requirement for butanol purification is 11.05 MJ/kg butanol.

Table 2

Economic evaluation of the hybrid separation system (mesitylene)

Item description (unit)	Extractor	COL - 1	COL – 2	COL - 3	COL - 4	Total
Shell / [10^3 US$]	294.7	1246.5	281.4	363.4	30.72	2216.72
Trays / [10^3 US$]	25.5	196.2	27.1	38.3	1.22	288.32
Condenser / [10^3 US$]	-	640.9	480.8	690.4	12.81	1824.91
Reboiler / [10^3 US$]	-	904.2	515.3	704.5	20.25	2144.25
Exchangers / [10^3 US$]	-	-	-	-	-	431.61
Heating / [10^3 US$/year]	-	3185.9	478.9	1216.9	9.92	4891.91
Cooling / [10^3 US$/year]	-	130.8	41.5	69.1	0.72	336.12
TAC / [10^3 US$/year]	106.7	4050.9	955.4	1746.7	30.9	6890.6

Table 3 presents the economic evaluation of separation sequence which uses 2-ethyl-1-hexanol as solvent. The operating cost (OPEX) of this process is

$3004.6 \cdot 10^3$ US$/year and the capital cost (CAPEX) is $5538.4 \cdot 10^3$ US$, which gives a total annual cost of $4659.9 \cdot 10^3$ US$/year. The energy requirement for butanol purification is evaluated at 6.76 MJ/kg butanol.

Table 3

Economic evaluation of the hybrid separation system (2-ethyl-1-hexanol)

Item description (unit)	Extractor	COL - 1	COL – 2	COL - 3	Decanter	Total
Shell / [10^3 US$]	188.4	406.5	595.4	281.5	25.9	1497.7
Trays / [10^3 US$]	15.0	44.4	74.1	27.2	-	160.7
Condenser / [10^3 US$]	-	281.1	745.1	501.9	326.1	1854.2
Reboiler / [10^3 US$]	-	454.5	918.5	595.6	-	1968.6
Exchangers / [10^3 US$]	-	-	-	-	-	57.2
Heating / [10^3 US$/year]	-	882.3	1006.1	931.9	-	2820.3
Cooling / [10^3 US$/year]	-	41.8	84.0	42.3	12.9	184.3
TAC / [10^3 US$/year]	67.8	1235.9	1867.7	1358.3	130.2	4659.9

Table 4 shows the economic evaluation of heat integrated DWC separation sequence which uses 2-ethyl-1-hexanol as solvent. The operating cost (OPEX) of this process is $1788.9 \cdot 10^3$ US$/year and the capital cost (CAPEX) is $3438.35 \cdot 10^3$ US$, which gives a total annual cost (TAC) of $3029.8 \cdot 10^3$ US$/year. The energy requirement for butanol purification is 4.46 MJ/kg butanol.

Table 4

Economic evaluation of the heat integrated DWC flowsheet (2-ethyl-1-hexanol)

Item description (unit)	**Extractor**	**DWC**	**DC**	**COOL**	**Decanter**	**Total**
Shell / [10^3 US$]	188.4	659	174.2	-	38.2	1059.8
Trays / [10^3 US$]	15.0	84.6	14.1	-	-	113.7
Condenser / [10^3 US$]	-	665.5	390.7	189	-	1245.2
Reboiler / [10^3 US$]	-	576.5	350.29	-	-	926.79
Exchangers / [10^3 US$]	-	-	-	-	-	92.86
Heating / [10^3 US$/year]	-	1245.2	413.9	-	-	1659.1
Cooling / [10^3 US$/year]	-	70.4	31.2	27.5	-	129.1
TAC / [10^3 US$/year]	67.8	1977.5	754.99	123.9	12.7	3029.8

7. Conclusions

The purification of butanol in a hybrid liquid-liquid extraction - distillation system can significantly reduce the energy requirement and the total annual cost. In this paper, two separation agents were used for liquid – liquid extraction columns (mesitylene and 2-ethyl-1-hexanol). The acetone-butanol-ethanol (ABE) mixture is normally recovered from the fermentation process with impurities as

acetic acid and butyric acid. Considering these impurities in the feed mixture with ABE, the downstream processing becomes difficult. This happens because of the high-boiling azeotrope formed by mesitylene and butyric acid. However, two conventional hybrid separation sequence were designed, optimized and economically evaluated. The best results were obtained by using 2-ethyl-1-hexanol as separation agent.

The conventional hybrid separation sequence which uses mesitylene as separation agent is an energy intensive process (11.05 MJ/kg butanol with a TAC of $6890.6 \cdot 10^3$ US$/year), due to the high amount of solvent used and the existence of the mesitylene-butyric acid azeotrope. The solvent loss with this azeotrope is around $424 \cdot 10^3$ kg/year which means $1695 \cdot 10^3$ US$/year loss. However, the energy requirement when using 2-ethyl-1-hexanol as a solvent is much lower - 6.76 MJ/kg butanol with a TAC of $4659.9 \cdot 10^3$ US$/year. A new, alternative heat integrated process has also been studied for the conventional separation sequence which uses 2-ethyl-1-hexanol. This process design uses a dividing-wall column to integrate two conventional columns in a single one. Thereby, the total annual cost is reduced to $3029.8 \cdot 10^3$ US$/year and the energy requirement is minimized to 4.46 MJ/kg butanol.

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