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DESIGN AND ECONOMIC EVALUATION OF A PROCESS FOR N-BUTYL ACRYLATE PRODUCTION

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The n-butyl acrylate is conventionally produced in batch reactors catalyzed by strong acidic homogeneous catalysts. To overcome corrosion, purification of product from catalyst, and large watery wastes, research based on solid catalysis received increased attention in the recent years. However, design and economic evaluation of an entire plant is scarce. In this view, two process alternatives based on solid catalysis are designed and evaluated. Aspen Plus is used as efficient CAPE tool. A plug flow reactor using Amberlyst 131 is proposed. One of the alternatives employs extractive distillation with ethylene glycol to separate the difficult acrylic acid / n-butyl acrylate mixture. The production and utility costs per metric ton of product are 1092 $/t, and 200 $/t, respectively.

Keywords: acrylic acid, esterification, n-butanol, reactor-separation-recycle

1. Introduction

The n-Butyl Acrylate (n-BA) is a derivative of acrylic acid (AA). It is an important bulk chemical having a wide range of applications. It is used in water-based paints [1], production of varnishes, adhesive, finishes of papers and textiles [2], and cleaning products, atmospheric surfactants, aqueous resins and elastomers [3]. A typical n-BA product purity, in weight percentages, is: >99.5 % n-BA, ≤0.05% water, and ≤0.01% AA [1].

The n-BA is produced in the equilibrium esterification reaction between AA and n-butanol (n-BuOH), obtaining water as by-product. This reaction can be catalyzed by homogeneous or heterogeneous catalysts. At commercial scale, n-BA is manufactured in a multi-stage process using two reactors employing homogeneous catalysis, as mentioned by Niesbach et al. [4]. Some homogeneous catalysts used are sulphuric acid and *p*-toluenesulfonic acid [1].

This four component system presents a complex thermodynamic behavior. According to Niesbach et al. [4], at 0.267 bar five azeotropes exist. AA is the only

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component completely miscible with water, while all the other present binary immiscibility gaps [4]. In the case of ternary mixtures, when water is present, the system presents immiscibility. Thus, the quaternary system is expected to present liquid-liquid immiscibility as well. Regarding kinetics, recent studies focus on solid catalysis using various ion exchangers ([5], [6], [7], [8]) and homogeneous catalysis using green solvents as reaction media [9].

In this study, the conceptual design and economic evaluation of a conventional Reactor-Separator-Recycle (RSR) system for n-BA production is developed. The design is for a plant with a capacity of 20,000 t/year of n-BA, operating 8,000 hours per year. The product specifications are ≥99.5% n-BA, ≤0.05% water, and ≤0.01% AA, by weight, while the rest is n-BuOH, which accounts as well for other impurities. The analysis starts with description of the chemistry, reaction kinetics, basic physical properties and thermodynamics. Then, the process design and steady state simulation follow. The mass and heat balance provides the basis for equipment sizing and cost calculations. The analysis ends with general conclusions on the proposed design. Aspen Plus is used as efficient CAPE tool.

2. Basis of design

The only reaction that takes place in the system is the esterification reaction (1) between n-BuOH and AA, obtaining the n-BA product and water as by-product. In practice, the secondary reactions (as polymerization of AA) are suppressed by the use of inhibitors [10]. Therefore, their influences on the overall process are not considered in the present study.

$$AA + n\text{-}BuOH \overset{cat}{\rightleftarrows} n\text{-}BA + Water \tag{1}$$

This is an equilibrium limited reaction that can be performed in liquid phase using solid catalysts. Based on laboratory experiments using a as solid catalyst Amberlyst 131 and assuming the LHHW mechanism, the following rate expression, and its parameters are proposed to describe the formation of n-BA [6]:

$$r = \frac{c_{cat} k_f K_{acid} K_{alcohol} \left(a_{acid} a_{alcohol} - (1/K_{eq}) a_{ester} a_{water} \right)}{\left(1 + K_{acid} a_{acid} + K_{alcohol} a_{alcohol} + K_{ester} a_{ester} + K_{water} a_{water}\right)^2} \tag{2}$$

$$k_f = k_0 \exp\left(-\frac{E_A}{RT} \right) \tag{3}$$

$$K_{eq} = \exp\left(2134/T - 1.799\right) \tag{4}$$

$$\ln\left(K_i\right) = A_i + B_i / T \tag{5}$$

Where r is the reaction rate in kmol/(m^3·s) and c_{cat} is the catalyst concentration in kg/m^3 of catalyst. a_i, *(i = acid, alcohol, ester, water)*, are the liquid phase activities, while K_{eq} is the equilibrium constant. The pre-exponential factor in the Arrhenius equation is k_0 = 227522 kmol/(kg·s) and the activation energy E_A = 57420641 J/kmol. The adsorption constants K_i, *(i = acid, alcohol, ester, water)*, of the four components are derived from the experimental data presented in the same reference [6]. It is assumed that the adsorption step is temperature dependent and follows the form of equation (5). The experimental data are presented in Table 1. The parameters *A* (intercept) and *B* (slope) of the adsorption equation are determined by regression, and are presented in Table 2.

Table 1

Experimental data of adsorption constants as function of temperature (abridged from [6] – LHHW mechanism)

T / [K]	*K* / [-]			
	AA	n-BuOH	n-BA	Water
338	1.126	0.979	0.292	6.946
348	1.003	0.878	0.276	6.113
358	0.777	0.764	0.243	5.567

Table 2

Regression parameters A and B of adsorption constant equation

Parameter	AA	n-BuOH	n-BA	Water
A	- 6.4719	- 4.4473	- 4.4937	- 2.0325
B	2235.8	1498.1	1107.0	1340.6

The UNIQUAC-HOC model and the two sets of binary interaction parameters as given in reference [4] are used. One set of parameters is used in vapour-liquid, while the second in liquid-liquid calculations. One of the design alternatives developed here makes use of ethylene glycol (EG). n-BuOH/EG and water/EG pairs are available in the Aspen Plus databanks. The AA/EG and n-BA/EG pairs are estimated from group contributions using the UNIFAC-LL method in Aspen Plus.

Pure component physical properties of all components in this system are available in Aspen Plus database. However, to describe the vapor pressure of AA and n-BA, we choose to use different sets of parameters for the Antoine equation. The parameters are regressed from experimental data from reference [1] and [11], for AA and n-BA, respectively. In the Antoine equation (6) the vapor pressure is expressed in bar, while temperature is in °C.

$$P_{vap,i} = \exp\left[C_{1,i} + C_{2,i} / \left(C_{3,i} + T\right)\right] \tag{6}$$

The regression is made using Aspen Plus, selecting the maximum-likelihood as objective function and using the default settings and calculation algorithm. The regressed parameters are presented in Table 3. A comparison between the experimental and calculated vapor pressure as function of temperature is presented in Fig. 1. A satisfactory fit is observed.

Table 3

Regression parameters C_1, C_2 and C_3 of Antoine equation

Component	C_1 / [-]	C_2 / [°C]	C_3 / [°C]
AA	9.75005	- 3624.1	233.2
n-BA	8.25679	- 2605.0	167.7

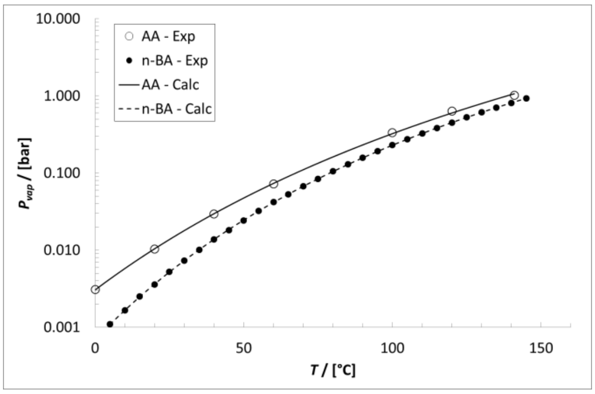

Fig. 1 Comparison between experimental and calculated vapour pressure data

The design of the separation system makes use of the phase equilibrium diagrams, which can be easily created in Aspen Plus. The separation between AA and n-BA is difficult due to their small relative volatility. Moreover, at 1.013 bar, the homogeneous azeotrope AA/n-BA that has a higher boiling point than n-BA, prevents obtaining pure n-BA as bottom product when distillation is employed. However, at 4 bar, the azeotrope disappears and separation by simple distillation is possible. Another option is based on the affinity of EG towards AA, which alters the relative volatility of the AA/n-BA binary system. Thus it can be used as solvent to separate AA from n-BA. AA/EG and n-BuOH/n-BA separation are relatively easy. The heterogeneous mixtures are separated by decanting. The liquid-liquid equilibrium is extensively described by reference [4], including comparison with experimental data.

3. Reactor design

The reactor design is made in the context of the RSR system (complete plant structure), and not designed as standalone equipment, as depicted in Fig. 2. The fresh feeds of n-BuOH ($F_{n\text{-}BuOH,0}$) and AA ($F_{AA,0}$), together with the recycle streams of unconverted reactants, are fed to the reactor. The reactor product is sent to separation where product n-BA, by-product water and the recycle streams are obtained. Depending on physical properties and separation choice, one or two recycle streams can be present. Thus, two distinct processes are developed.

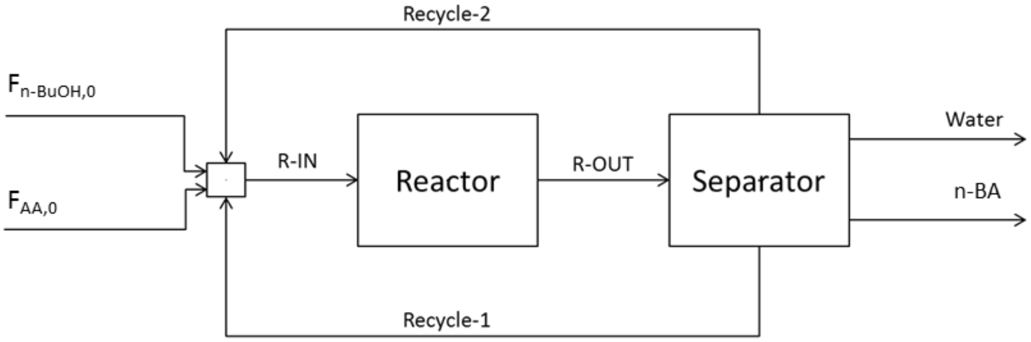

Fig. 2. Reactor-Separation-Recycle structure

The separation section of the first system is modeled as a black-box at given separation factors (separation factor, β = fraction of component in the inlet stream entering the separation section and leaving the plant as product): $\beta_{n\text{-}BuOH} = 0$, $\beta_{AA} = 0$, $\beta_{Water} = 0.9$, $\beta_{n\text{-}BA} = 0.25$. It can be observed that the recycled fraction of n-BA is quite high. This is due to the difficult separation AA/n-BA.

For the second system, the separation factors hold as well. However, it is expected that less n-BA is recycled. This is because extractive distillation favors the AA/n-BA separation. Thus, a separation factor $\beta_{n\text{-}BA} = 0.75$ is selected. Since two recycles are present, the recycled n-BA is equally split. 0.125 goes with one recycle, 0.125 with the other, while 0.75 is removed from the system. Water, being the lightest component, is recycled with n-BuOH (Recycle-2).

A conversion of 55% AA is selected in order to keep a balance between reactor size (amount of catalyst) and recycle flow rate (unconverted reactants). Due to plant controllability reasons, the molar ratio n-BuOH : AA at the reactor inlet is selected to be 3.1 and 4.5 for the one recycle and two recycle system, respectively. The nominal flow rate of AA and n-BuOH are fed in such amounts that meet the production capacity. Given these specifications, the amount of required catalyst is 2,000 kg. The reactor selected is a multi-tubular heat exchanger-like equipment with the catalyst inside the tubes. Given a bed voidage of 0.5 and catalyst particles of 0.75 mm in diameter with a density of 740 kg/m^3, the volume that accommodates the catalyst amount is calculated. Finally, the reactor has 57 tubes with diameters of 0.2 m and 3 m in length.

Given the reactor dimensions (amount of catalyst) and the separation targets of the separation system, a preliminary material balance is obtained as presented in Table 4 and Table 5, respectively. Based on these, the design of the separation system is made.

Table 4

Preliminary mass balance of the RSR system with one recycle

Stream	$F_{AA,0}$	$F_{n\text{-}BuOH,0}$	*R-IN*	*R-OUT*	*Recycle-1*	*n-BA*	*Water*
Mole Flow/[kmol/h]	20	20	220	220	180	20	20
Mole Fraction							
Water			0.010	0.101	0.012		1
n-BuOH		1	0.542	0.451	0.551		
AA	1		0.176	0.085	0.104		
n-BA			0.273	0.364	0.333	1	
Mass Flow/[kg/h]	1441	1482	19346	19346	16422	2563	360
Mass Fraction							
Water			0.002	0.021	0.002		1
n-BuOH		1	0.456	0.380	0.447		
AA	1		0.144	0.069	0.082		
n-BA			0.398	0.530	0.468	1	

Table 5

Preliminary mass balance of the RSR system with two recycles

Stream	$F_{AA,0}$	$F_{n\text{-}BuOH,0}$	*R-IN*	*R-OUT*	*Recycle-1*	*Recycle-2*	*n-BA*	*Water*
Mole Flow/[kmol/h]	20	20	272	272	48	184	20	20
Mole Fraction								
Water			0.008	0.082		0.012		1
n-BuOH		1	0.632	0.558		0.825		
AA	1		0.140	0.066	0.376			
n-BA			0.220	0.294	0.624	0.163	1	
Mass Flow/[kg/h]	1441	1482	23217	23217	5146	15147	2563	360
Mass Fraction								
Water			0.002	0.017		0.003		1
n-BuOH		1	0.549	0.485		0.744		
AA	1		0.118	0.056	0.253			
n-BA			0.331	0.442	0.747	0.254	1	

4. Design of the separation system

System with one recycle. The process flowsheet is presented in Fig. 3. The reactor outlet stream (*R-OUT*, Table 4) contains about 2.1% water, while the remaining is organics: 38.0% n-BuOH, 6.9% AA and 53.0% n-BA – all by weight. As water forms three azeotropes (one ternary, and two binary with n-BuOH and n-BA) all of them being the first singular points in the system having the lowest boiling points, it is expected that it can be removed first. This is achieved in a reboiled stripping column (C-1) where the ternary azeotrope is obtained as top vapor. After vapor condensation (COND-1) and liquid-liquid phase separation (LL-SEP), the aqueous phase is partially vaporized (VL-SEP) and liquid water (97.7%) is removed from the system. The vapors containing n-BuOH are recycled to the reaction section. The organic phase is fed as reflux back to C-1. The bottom stream of C-1 is fed to a distillation column (C-2). n-BA is obtained as bottoms product (99.5%), while a mixture containing AA, n-BuOH and a significant amount of n-BA is recycled to the reaction section.

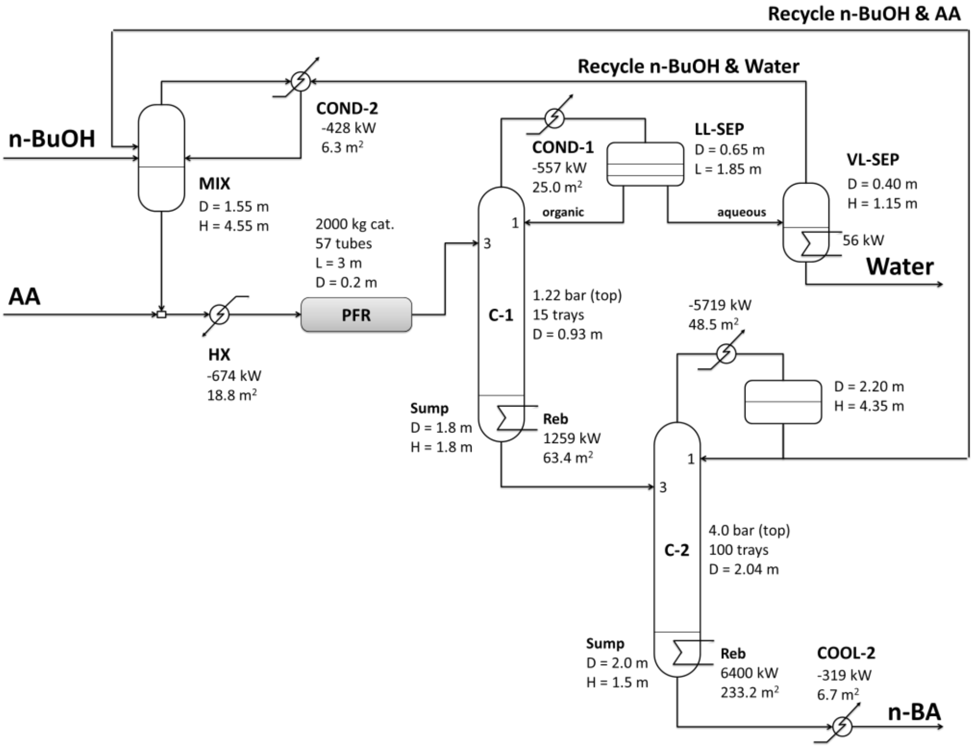

Fig. 3 Process flow diagram of the system with one recycle

Details on the temperature and concentration profiles are showed in Fig. 4. As the reaction is slightly endothermic, the temperature decreases only with 2.5 °C along the reactor length (top-left diagram). This profile also suggests that most of the reaction takes place in the first half of the reactor; this can be observed by the concentration profiles. AA conversion is 49.96%. Along the column C-1 (top-right diagram), water decreases from top to bottoms, down to the desired specification. In column C-2 (bottom diagram), the desired specification of n-BA is reached in the bottoms but with small changes in concentrations from tray to tray, as also suggested by the temperature profile.

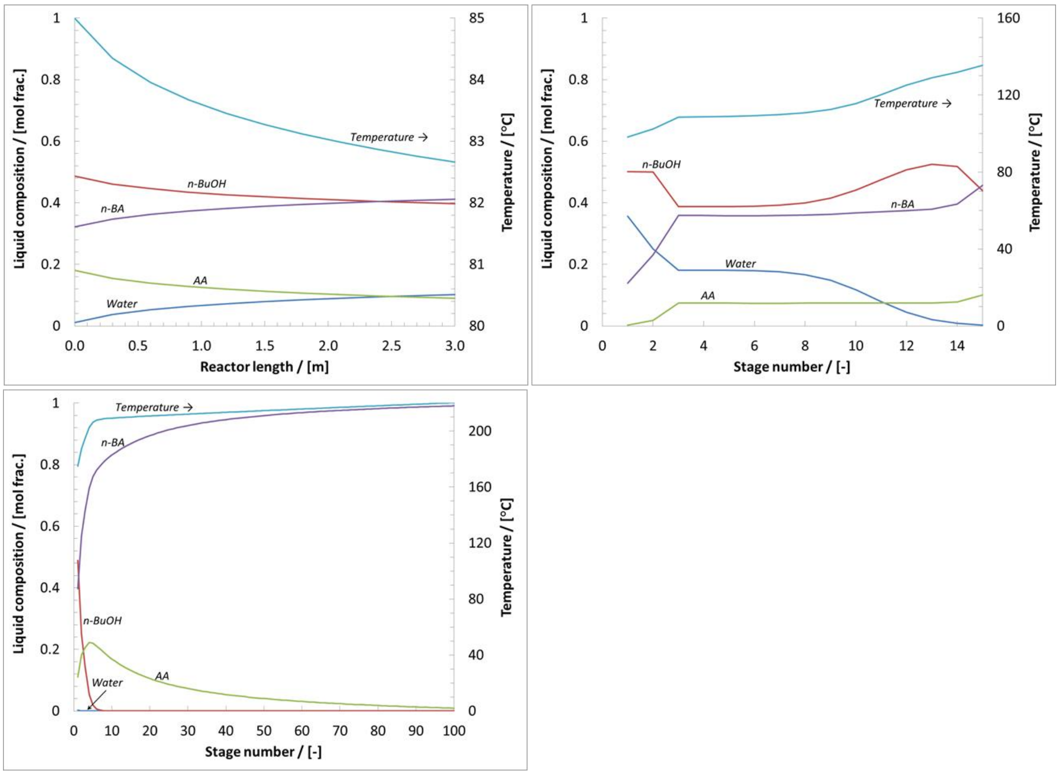

Fig. 4 Temperature and concentration profiles (system with one recycle); Top-left: reactor, Top-right: C-1, Bottom: C-2

System with two recycles. An alternative to separate n-BA from the n-BuOH/AA/n-BA mixture is to use extractive distillation. Ethylene glycol seems to be a suitable solvent to extract AA from this ternary mixture. The process flowsheet is presented in Fig. 5. An extractive distillation column (C-3) is employed. The n-BA recovery in the C-3 is 0.94, 0.85 in C-2, while the overall recovery of the entire separation system is $\beta_{n\text{-}BA} = 0.80$. Thus, as expected, a lower fraction of n-BA is recycled to the reaction section.

The reactor outlet stream (*R-OUT*, Table 5) contains about 1.7% water, 48.5% n-BuOH, 5.6% AA and 44.2% n-BA – all by weight. Since this is a mixture very similar with the one from the one recycle system, the water is removed in the same manner. The bottom of C-1 is fed to the extractive distillation column C-3. EG extracts AA and caries it in the bottoms while n-BA and n-BuOH are obtained as distillate. The separation of AA from this ternary mixture is almost complete. 99.5% found in the feed is separated from the solvent by distillation (C-4) and then recycled to the reaction section. The split between AA and EG is easy. The n-BuOH/n-BA mixture can be easily separated in a distillation column (C-2). n-BA is obtained as bottoms product, while n-BuOH and some n-BA are obtained as distillate.

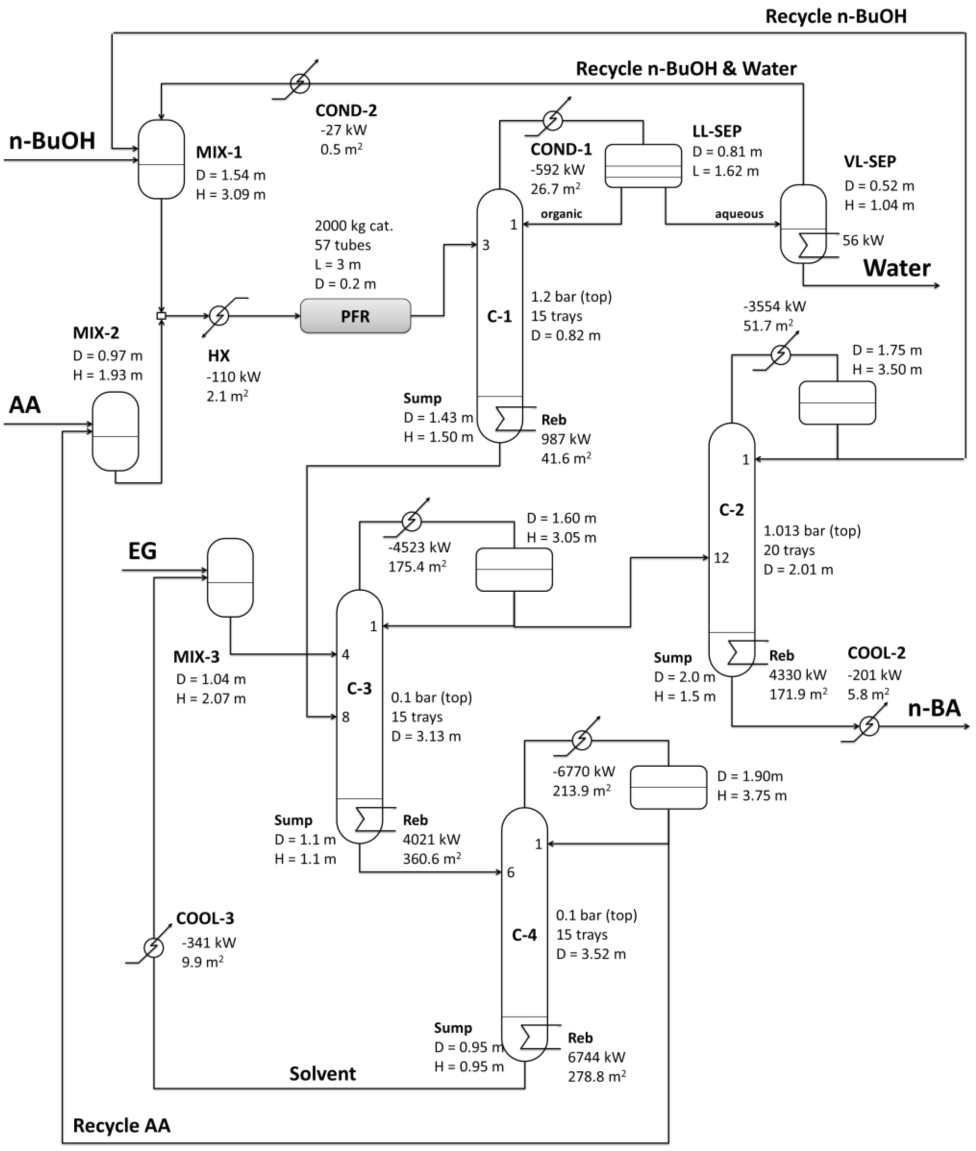

Fig. 5 Process flow diagram of the system with two recycle (without counting the solvent recycle)

Details on the temperature and concentration profiles are showed in Fig. 6. In reactor (top-left diagram), similar profiles as in the system with one recycle are observed. However, in absolute values the concentrations are different since less n-BA is recycled. The AA conversion is 54.96%. The profiles in C-3 (bottom-right diagram) show how AA is separated from the mixture. The distillate needs to be free of AA as it will end up in the product stream if escapes in the distillate. Since the AA/n-BA split is already made, the n-BuOH/n-BA is easily split in C-2 (bottom-left diagram).

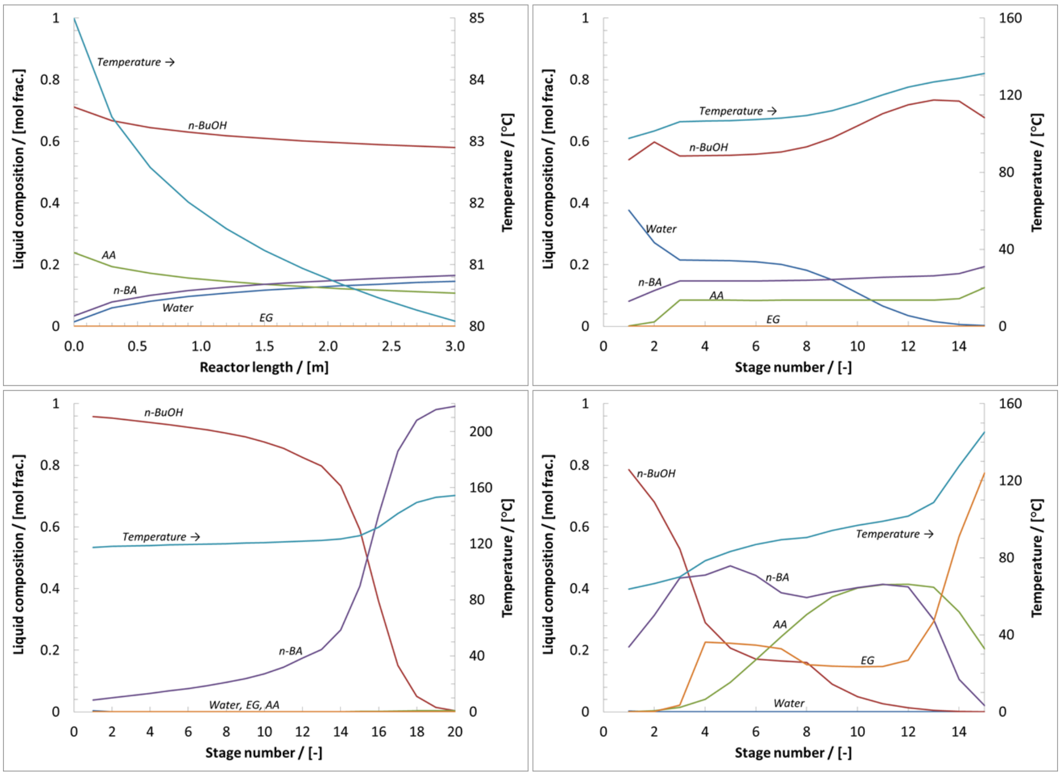

Fig. 6 Temperature and concentration profiles (system with two recycles); Top-left: reactor, Top-right: C-1, Bottom-left: C-2, Bottom-right: C-3

Equipment sizing. The sizing of the main equipment is made based on the material and energy balance of the steady-state simulations. The columns diameters are sized using the facilities of Aspen Plus. The sumps and reflux vessels are sized based on a residence time of 10 min. The mixers, settlers and flash vessels are sized based on 10 min residence time and the half-full criteria. All heat exchangers are designed based on a heat transfer coefficient of 700 kcal/(m^2h·K). For coolers and condensers, cooling water of 20 °C is used, while for reboilers, steam of 6 or 11 bars. The reactor is a multi-tubular heat exchanger-like equipment, and its area is calculated based on its tubes that accommodate the amount of catalyst. The main dimensions and some operating parameters, for both processes, are given in Fig. 3 and Fig. 5, respectively.

5. Economic analysis

Calculation basis. The components of the economic potential (EP) calculations, equation (7), of the acrylate process are cost of product (n-BA) and reactants (AA and n-BuOH), cost of utility (steam, cooling water, and waste water treatment) and amortization cost of capital expenditures (major equipment items).

All costs are in \$/year. The calculations are made based on cost indices for 2011, including the prices of AA, n-BuOH and n-BA.

Besides the EP, other key indicators can be calculated to judge upon process performance, and to some extent, for comparison purposes with other data reported in literature. Here, the production cost ($C_{SpecProd}$ - equation (8)) and specific utility consumption ($C_{SpecUtility}$ - equation (9)) per ton of product are calculated, both in \$/t of product.

$$EP = C_{Product} - C_{Reactants} - C_{Utilities} - C_{Amortization} \tag{7}$$

$$C_{SpecProd} = \left(C_{Reactants} + C_{Utilities} + C_{Amortization}\right) / P_{n-BA} \tag{8}$$

$$C_{SpecUtility} = C_{Utilities} / P_{n-BA} \tag{9}$$

$$C_{Amortization} = C_{CapEx} / \text{payback period} \tag{10}$$

$P_{n\text{-}BA}$ is the annual production in t/year. Reference [4] provides the price of AA, 614.5 €/t, calculated based on data from other reference[4]. The same reference provides the prices for n-BuOH, 628.8 €/t, and n-BA, 1350 €/t. To transform in US\$, a factor of 1.11 \$/€ is used.

The cost of utilities is calculated based on requirements of steam, cooling water and waste water, and their associated specific costs. These requirements are easily available from the mass and heat balance calculated by Aspen Plus. The specific cost of steam, cooling water and waste water are 7.78 (6 bar) or 8.22 (11 bar) \$/GJ, 0.72 \$/GJ and 0.5 \$/kg$_{\text{organics}}$, respectively.

The amortization cost ($C_{Amortization}$, in \$/yr) is the installed cost of major equipment (C_{CapEx}) over a payback period of three years (10).

The basic equipment dimensions provide the input for the cost equations of equipment, together with the material of construction and operating pressure. All equations are taken from a single reference [12].

The installed cost of vessels and columns (shells) is calculated with equation (11). $M\&S$ is the Marshall and Swift equipment cost index (M&S = 1536.5 for 2011), D and H are diameter and height in meters, F_m is the material factor (F_m = 1 for CS, 2.25 for SS) and F_p is the pressure factor ($F_p = 1 + 0.0074(P - 3.84) + 0.00023(P - 3.48)^2$). The installed cost of column trays is calculated using equation (12). F_t is the tray factor (F_t = 0 for sieve trays, 0.6096 m spacing), F_m is the material factor (F_m = 0 for CS, 1.7 for SS) and N_T is the number of trays. For installed costs of shell and tubes heat exchangers, equation (13) is used. The tubular reactor is a shell and tube-like equipment and its installed cost is calculated using the same equation. In addition, the cost of catalyst is taken as 50

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[4] Bell, S.L., 2003, Acrylic Acids and Esters, Report No. 6D, California

\$/kg [13]. F_m is the correction factor for material (F_m = 1 for CS/CS, 2.81 for CS/SS, and 3.75 for SS/SS), F_d is the correction for design type (F_d = 0.8 for fixed-tube sheet, 1.35 kettle reboiler) and F_p is the correction for the design pressure (F_p = 0 for design pressures less than 10 bar).

$$C_{Vessels/Columns} = \left(M\,\&\mathrm{S}/280\right)\left(957.9D^{1.066}H^{0.82}\right)\left(2.18+F_mF_p\right) \tag{11}$$

$$C_{Trays} = \left(M\,\&\mathrm{S}/280\right)97.2D^{1.55}\left(F_t+F_m\right)N_T \tag{12}$$

$$C_{HX} = \left(M\,\&\mathrm{S}/280\right)\left(474.7\cdot A^{0.65}\right)\left(2.29+F_m\left(F_d+F_p\right)\right) \tag{13}$$

System with one recycle. The results obtained following the calculation basis are showed in Table 6, namely the cost components of the economic potential and performance indicators. Operating at nominal capacity, the product sales bring about 30.6 million \$ yearly. For manufacturing the product, 16.1 million are spent on raw materials, 2.3 on utilities, and 1.5 on amortization of capital investment. The sum of these costs, 19.8 million \$, represent the production cost (81.1% raw materials, 18.6% utilities, and 7.3% amortization). A breakdown of utility costs shows that 91.6% is allocated to steam consumption, 6.9% to cooling water, and only 1.5% to waste water treatment. Regarding amortization costs, 64.8% is spent on columns, including sumps, 23.5% on heat exchangers, 8.0% on reactor, including catalyst, and 3.7% on other vessels.

Table 6

Cost components of the economic potential (left) and key performance indicators (right) for the process with one recycle

Cost component	Value	Performance Indicator	Value
$C_{Product}$ / \$/yr	30,602,000	EP / \$/y	10,756,000
$C_{Reactants}$ / \$/yr	16,101,000	$C_{SpecProd}$ / \$/t	973
$C_{Utilities}$ / \$/yr	2,294,000	$C_{SpecUtility}$ / \$/t	113
$C_{Amortization}$ / \$/yr	1,451,000		

Subtracting the production costs from the product sales gives an economic potential of 10.8 million \$ yearly. The production cost per ton of product is about 973 \$ (876 €), while the utility cost per ton of product is roughly 113 \$ (101 €).

System with two recycles. For this system, the main results are showed in Table 7, namely the cost components of the economic potential and performance indicators. The product sales bring about 30.7 million \$ yearly. For manufacturing the product, 16.2 million are spent on raw materials, 4.1 on utilities, and 2.1 on amortization of CapEx. The sum of these costs, 22.4 million \$, represent the production cost (72.3% raw materials, 18.3% utilities, and 9.4% amortization). A breakdown of utility costs shows that 91.0% is allocated to steam consumption, 8.1% to cooling water, and only 0.9% to waste water treatment. Regarding amortization costs, 42.3% is spent on columns, including sumps, 49.3% on heat exchangers, 5.5% on reactor, including catalyst, and 2.9% on other vessels.

Table 7

Cost components of the economic potential (left) and key performance indicators (right) for the process with two recycles

Cost component	Value	Performance Indicator	Value
$C_{Product}$ / \$/yr	30,758,000	EP / \$/y	8,366,000
$C_{Reactants}$ / \$/yr	16,179,000	$C_{SpecProd}$ / \$/t	1,092
$C_{Utilities}$ / \$/yr	4,106,000	$C_{SpecUtility}$ / \$/t	200
$C_{Amortization}$ / \$/yr	2,107,000		

Subtracting the production costs from the product sales gives an economic potential of 8.4 million $ yearly. The production cost per ton of product is about 1092 $ (983 €), while the utility cost per ton of product is roughly 200 $ (180 €).

6. Conclusions

Large scale production of n-BA based on solid catalysts is feasible. Two conventional reactor-separator-recycle processes are designed, each producing 20,000 t/yr of n-butyl acrylate. Both employ a catalytic fixed-bed reactor using Amberlyst 131. The reactants are recycled together or separately, depending on the structure of the separation system. Particularly difficult is the AA/n-BA separation. The system with one recycle makes the split by conventional distillation. The two recycle system makes the split by extractive distillation using ethylene glycol. The latter is to some extent better, since it overcomes some drawbacks of the former process: a more realistic design of the separation system, lower n-butyl acrylate recycle, and operation at lower temperatures.

From an economic perspective, the first process presents higher economic potential and key performance indicators. However, a closer look reveals that the differences are not that large to conclude that the first process is by far more attractive. This is because the economics are raw materials driven, as their costs are by far the highest compared with utilities and amortization costs. For example, the difference between the two economic potentials of each process is about 2.4 million $, whereas their absolute values are 10.8 and 8.4, respectively. Moreover, the overall production costs per ton of product are 973 and 1,092 $, respectively.

The production cost per ton of product, for both processes, is comparable with similar costs reported in literature. For two optimized processes based on reactive distillation, Niesbach et al. [4] reports a production cost of 1192 and 855 €/t, respectively. This is roughly 1324 and 950 $/t, similar with those reported in this study.

R E F E R E N C E S

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