Analysis of the energy efficiency of some butanol recovery processes

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This work presents an energetic analysis of three butanol recovery processes from acetone-butanol-ethanol (ABE) fermentation broth. The processes were based on: 1) gas stripping, 2) liquid-liquid extraction, and 3) supercritical extraction. Material and energy balance simulations were carried out by commercial software Aspen Plus®. Processes were characterized in terms of energy efficiency and specific energy requirement. Operating conditions – e.g. gas stripping flow rate and solvent flow rate - were investigated and optimized with respect to the energy objective functions.

1. Introduction

Butanol is a building block of chemicals and a promising biofuel. It may be produced according to the biotechnological route from renewable resources. Indeed, the acetone-butanol-ethanol (ABE) fermentation by clostridia is a promising eco-sustainable process, provided that production costs are reduced (Qureshi et al., 2008). Issues that play a key role in the production cost are: the feedstock; the fermentation system (strain and bioreactor); and the butanol recovery/concentration step from the fermentation broth. A potential solution for the feedstock cost is the adoption of lignocellulosic biomass as resource. Indeed, the lignocellulosic biomass is a low cost, low social impact feedstock and *Clostridium* strains are able to metabolize the spectrum of carbohydrates typically produced by the pretreatment-hydrolysis processes (Raganati et al., 2015; Raganati et al., 2012). The butanol recovery/concentration step is made particularly complex by the low concentration of solvents in the fermentation broth (< 2%wt) due to the toxicity/inhibition of butanol to the cell. As a consequence, the separation of butanol from fermentation broths by using ordinary steam distillation is infeasible because it could require more energy than the energy content of the recovered butanol (Qureshi et al., 2005).

Various recovery/concentration methods are reported in the literature with the aim to reduce the energy request for butanol mass unit produced by the biotechnological route. The reported methods include gas stripping, vacuum flash, liquid-liquid extraction, supercritical extraction, membrane solvent extraction, membrane pervaporation, and adsorption (Huang et al., 2014).

This contribution reports results of simulations aimed to assess the energy efficiency of three butanol recovery flowsheets based on: 1) gas stripping (GS); 2) liquid-liquid extraction (LL-E); and 3) supercritical extraction (SE). Operating conditions such – e.g. gas stripping flow rate and solvent flow rate - were investigated and optimized with respect to energy objective functions.

2. Methodology

The simulations were performed under stationary conditions by using the commercial software Aspen Plus®. Fermentation broth was modelled as a stream of water, butanol, acetone, and ethanol. The broth was at 30°C and 1 atm. Table 1 reports the composition of the fermentation broth simulated in this work. 2-butyl-1-octanol was selected as solvent for extractive ABE removal (González et al., 2014). The broth was modelled as a butanol/water mixture (butanol mass fraction x_B=0.018) in the supercritical extraction simulations.

Table 1: Broth composition and mass flow rate: broth mass flow rate 10,000 kg/hr

	Butanol	Acetone	Ethanol	Water
Mass fraction (-)	0.018	0.009	0.003	0.9700
Mass flow rate (kg/hr)	180	90	30	9700

2.1 Property Method

Thermodynamic properties of the butanol/water and ABE/water systems were determined according to the property method NRTL-HOC. This method allowed to reproduce accurately the experimental data of vapour-liquid equilibrium reported in literature (Figure 1) according to Stockhardt and Hull. (1931).

The liquid-liquid equilibrium between the aqueous phase and the organic phase - rich in 2-butyl-1-octanol - was predicted by the distribution coefficient measured and reported in literature (González et al., 2014)

Thermodynamic properties of the butanol/water/CO_2 ternary mixture were assessed by the property method RK-ASPEN. The interaction parameters were set according to the regression of the experimental data reported in literature (Chen et al., 2002).
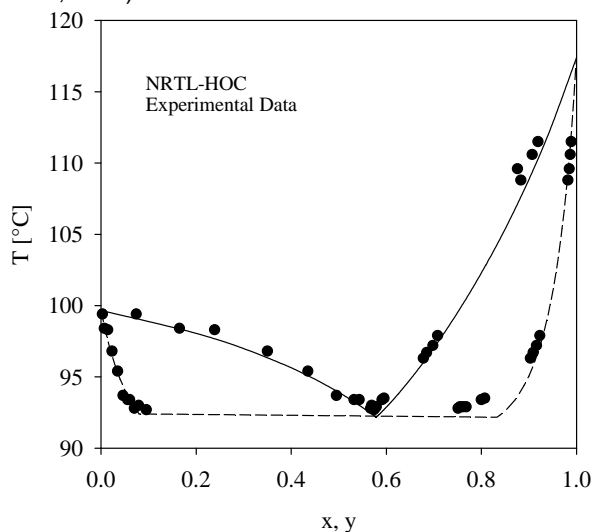

Figure 1: Vapour-Liquid equilibrium (VLE) data of butanol/water system at atmospheric pressure as a function of the mass fraction of butanol. Lines are plots of the NRTL-HOC thermodynamic model: dashed – liquid phase, continuous - vapour. Symbols are experimental data.

2.2 Flow sheet and model libraries

Figure 2 reports the flow-sheet of the butanol recovery process based on gas stripping.

For the sake of brevity only a simplified description of the flowsheets reported in Figure 2-4 will be carried out The broth was sent to the gas stripping column STRIPPER: the air stream stripped butanol, acetone, and ethanol from the broth. The gas stream from STRIPPER was delivered to a condenser operated at 0°C: a liquid ABE rich stream was separated from the air stream. The train of distillation column DIST-2 and DIST-3 recovered acetone and ethanol from the ABE rich stream: a butanol/water mixture was produced. The reflux ratio and the distillate flow rate of DIST-2 were tuned to attain the targets: acetone purity of 99.5%wt and acetone recovery of 99.5%. The reflux ratio and the distillate flow rate of the distillation column DIST-3 were tuned to attain the targets: butanol recovery of 99.5%wt and ethanol recovery of 95.0%. The butanol/water mixture from the column DIST-3 was delivered to an azeotropic distillation section to recovery butanol and water. The azeotropic distillation section was made of two stripping columns - one to strip butanol from water (DIST-4) and one to strip water from butanol (DIST-5) - and a liquid-liquid separator to process the condensed vapor leaving the two stripping columns. The liquid-liquid separator recovered the water rich phase, delivered to the column DIST-4, and the butanol rich phase, delivered to the column DIST-5. The bottom flow rate of the distillation columns were tuned to attain the targets: butanol purity of 99.5%wt and water purity of 99.5% wt.

The Figure 3 reports the flowsheet of the butanol recovery process based on liquid-liquid extraction. The broth was delivered to the liquid-liquid extraction column EXT: the solvent stripped the butanol, acetone, and ethanol from the broth. The solvent rich stream produced from EXT was delivered to a distillation column to separate the extraction solvent from the ABE mixture. The solvent stream was recycled to the extraction column and the ABE rich stream was delivered to a distillation train as presented for the process based on gas stripping.
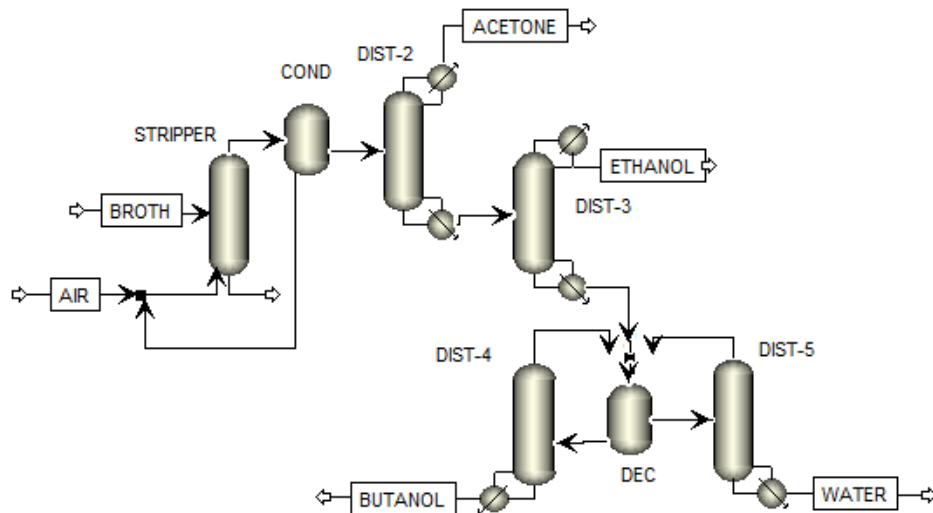
Figure 2: Flow-sheet of the butanol recovery process based on gas stripping
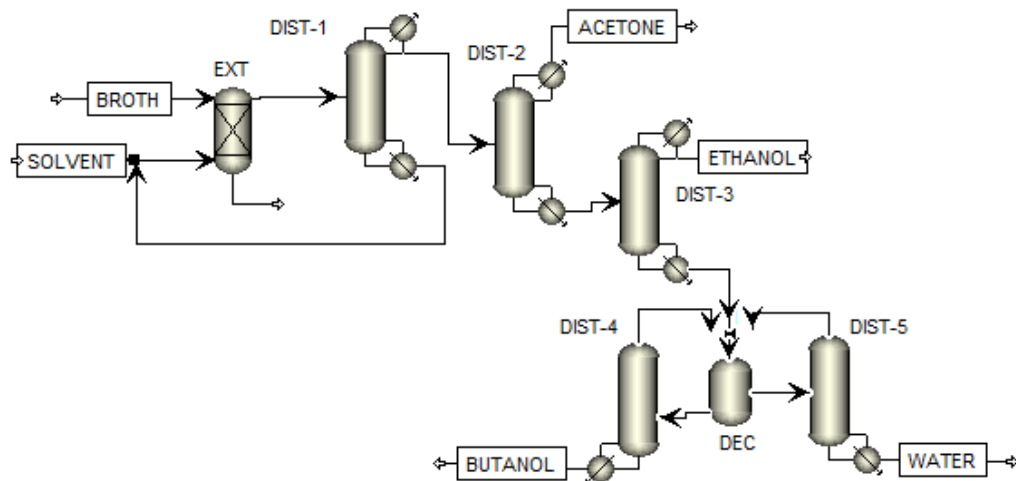

Figure 3: Flowsheet of the butanol recovery process based on liquid-liquid extraction

Figure 4 reports the simplified flow-sheet of the butanol recovery process based on CO_2 supercritical extraction. The butanol/water mixture separation section of the process was not reported. The broth - mixture of butanol and water - was compressed in a pump and delivered to the supercritical extractor SE (modelled as a vapour- liquid equilibrium unit). In the SE unit, supercritical CO_2 stripped the butanol from the broth. The solvent rich stream from SE was delivered to a flash unit to recovery butanol/water mixture from CO_2. The solvent stream was recycled to the supercritical extractor and the butanol/water mixture was sent to a product purification section (not considered in this work).
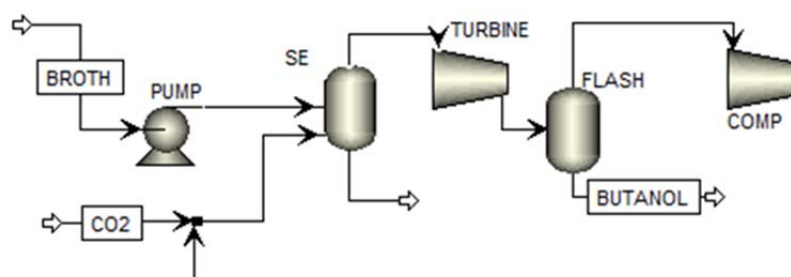

Figure 4: Flowsheet of the butanol recovery process based on CO_2 supercritical extraction

A heat integration scheme - not reported for the sake of brevity - was used in all the investigated processes to minimize the system energy requirements.

2.3 Objective functions

The specific energy requirement for butanol purification, E_D, is defined according to the equation:

$$E_D = \frac{Q}{m_{B-P} \cdot LHV_B} \tag{1}$$

where m_{B-P} is the mass flow rate of the butanol produced in the system, LHV_B the lower heating value of butanol, Q the total energy rate supplied to the process by utilities.

System energy efficiency, η, is defined according to the equation:

$$\eta = \frac{m_{B-P} \cdot LHV_B}{m_{B-F} \cdot LHV_B + Q} \tag{2}$$

where m_{B-F} is the mass flow rate of butanol fed to the system.

The energy required in the steps of the investigated flowsheets (heat, electricity, …) was made homogeneous and expressed as fuel equivalents. In particular, 1 MJ of electrical energy was set as 3 MJ of fuel-derived energy, 1 MJ of steam heat was set as 1.1 MJ of fuel-derived energy, 1 MJ of frigories was set as 1.1 MJ of fuel-derived energy. The coefficient of COP performance was assumed 3.

3. Results

Figure 5 reports η (a) and E_D (b) as a function of air molar flow rate n_{AIR} for the process based on gas stripping. The investigated objective functions as a function of n_{AIR} were characterized by non-monotonic behaviour. Indeed, the increase of n_{AIR} enhanced the separation driving force across the column and the amount of butanol recovered increased too. However, system heat duty increased too. The optimum value of n_{AIR} depended on the selected objective function.
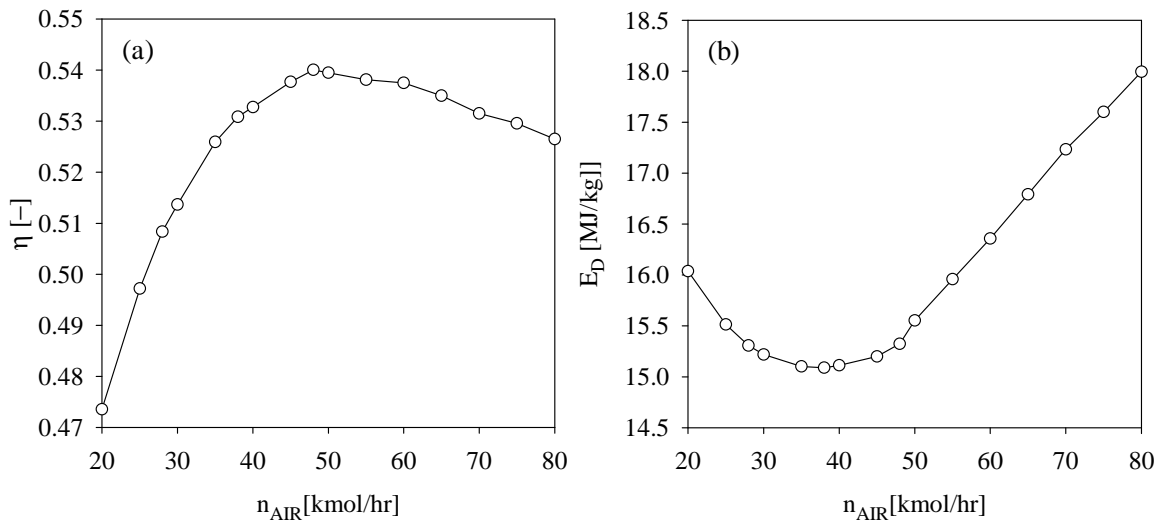

Figure 5. η (a) and E_D (b) as a function of n_{AIR} assessed for the system based on gas stripping.

Table 2 reports simulation results of butanol recovery process based on liquid-liquid extraction as a function of the mass ratio between solvent flow rate and broth fermentation flow rate S/F. As a general result, the increase of S/F increased both the butanol recovery and the system heat duty. As a result, η was characterized by a maximum at S/F equals to 0.18. E_D was characterized by a constant value for S/F smaller than 0.14 and increased significantly with S/F. The optimization of both objective functions occurred at S/F characterized by very low acetone recovery. As a consequence, the selection of S/F strictly depends on the required acetone recovery. The process optimization in this work was made by setting the acetone recovery at 0.7.

Table 3 reports a comparison between the simulation results of butanol recovery process based on supercritical extraction - in terms of butanol recovery α_{BUT} and butanol mass fraction in the raffinate stream at the outlet of supercritical extractor x_{B-R} – and experimental results reported by Moreno et al. (2012). P is the

supercritical extractor pressure, S/F is the mass ratio between the flow rate of solvent and broth fermentation, x_{B-F} the butanol mass fraction in the broth fed to the process. The agreement between experimental and simulated results was successful. Therefore, the simulated flowsheet was used for the further investigation.

Table 2: Simulation results of butanol recovery process based on LL extraction.

S/F	η	E_D	α_{BUT}	α_{AC}
0.04	0.30	3.99	0.31	0.05
0.10	0.69	4.11	0.75	0.12
0.14	0.82	4.26	0.92	0.16
0.18	0.86	4.50	0.98	0.21
0.20	0.86	4.64	0.98	0.23
0.30	0.85	5.40	0.99	0.33
0.40	0.83	6.29	0.99	0.44
0.50	0.80	7.73	0.99	0.54
0.60	0.77	9.28	0.99	0.65
0.70	0.75	10.57	0.99	0.74
0.80	0.73	11.73	0.99	0.83
0.80	0.73	11.73	0.99	0.83
0.90	0.70	13.21	0.99	0.89
1.00	0.69	14.39	0.98	0.94

Table 3: Butanol recovery process based on supercritical extraction

			Experimental data (*)		Simulated data	
x_{B-F}[%wt]	P [atm]	S/F	α_{BUT}	x_{B-R} [%wt]	α_{BUT}	x_{B-R} [%wt]
1.2	140	3.0	0.82	0.23	0.82	0.21
0.4	140	3.9	0.62	0.17	0.69	0.11

(*) Moreno et al. *(2012)*

Figure 6 reports η (a) and E_D (b) assessed for the system based on supercritical extraction. Data are reported as a function of S/F for several values of P. η and E_D are characterized by a non-monotonic behaviour with respect to both S/F and P. Indeed, an increase of S/F (or an increase of P) on the one hand enhance the amount of butanol recovered in the supercritical reactor, on the other hand enhance total energy required by the system. The optimum value of operating conditions depends on the objective functions considered and on the relative weight of the amount of butanol produced and system energy requirement. Optimization of η occurs at S/F and P values higher than ones of E_D.
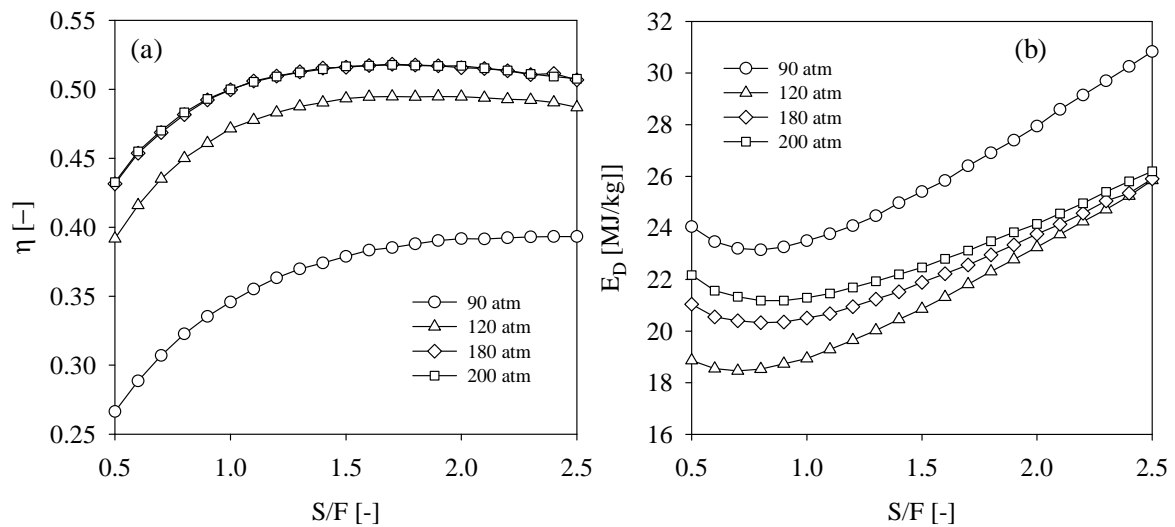

Figure 6: η (a) and E_D (b) as a function of the mass ratio between the flow rate of solvent and broth fermentation (S/F), parametric in the operating pressure (P) for the system based on supercritical extraction.

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Table 4 reports E_D and η assessed as optimal for the investigated butanol recovery processes. LL extraction process is characterized by the lowest energy requirements and the highest energy efficiency. Supercritical extraction process is characterized by the highest energy requirement and the lowest energy efficiency. This is due to the high energy required to pressurize fermentation broth and solvent under the selected operating conditions. In particular, the butanol recovery may play a key role in the energy efficiency assessment and further investigation is required.

Table 4: Optimal values of η and E_D for the investigated butanol recovery processes

Process	η	E_D
GS	0.54	15.3
LL-E	0.76	9.9
SE	0.52	18.4

4. Final remarks

An energetic analysis of butanol recovery processes from ABE fermentation broth has been developed and discussed. Three butanol recovery processes have been considered: 1) gas stripping, 2) liquid-liquid extraction, 3) supercritical extraction. Under the operating condition investigated the liquid-liquid extraction was characterized by the best performance in terms of energy recovery. Supercritical extraction process was characterized by the highest energy requirements and lowest energy efficiency due to the high energy input required to pressurize the fermentation broth.

The presented analysis should be always reported for the butanol recovery processes proposed in the literature. Moreover, the characterization over a wide interval of operating conditions for true fermentation broth should be included.

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