



Conceptual model-based optimization and environmental evaluation of waste solvent technologies: Distillation/incineration versus distillation/pervaporation



Regina Meyer^a, Danilo Alexander Figueroa Paredes^a, Mauren Fuentes^a, Antonio Amelio^b, Betzabet Morero^c, Patricia Luis^d, Bart Van der Bruggen^b, José Espinosa^{a,e,*}

^aINGAR (CONICET-UTN), Avellaneda 3657, 3000 Santa Fe, Argentina

^bDepartment of Chemical Engineering, Process Engineering for Sustainable Systems (ProCESS), KU Leuven, W. de Croijlaan 46, B-3001 Leuven, Belgium

^cINTEC (CONICET-UNL) Güemes 3450, 3000 Santa Fe, Argentina

^dMaterials & Process Engineering (iMMC-IMAP), Université Catholique de Louvain, Place Sainte Barbe 2, 1348 Louvain-la-Neuve, Belgium

^eUniversidad Nacional del Litoral, Facultad de Ingeniería Química, Santiago del Estero 2829, 3000 Santa Fe, Argentina

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ABSTRACT

In this work, a conceptual model-based optimization is performed for designing two waste solvent treatment technologies: (i) hybrid process distillation assisted by pervaporation and (ii) distillation/incineration.

This task was performed resorting to conceptual models or shortcuts for each unit operation involved, which are characterized by their abilities to capture the essence of the process at a low computational cost. Life cycle assessment (LCA) was applied to evaluate the environmental impact of both alternatives. Optimal values for the utilities, i.e., cooling water, electricity and steam needed for distillation and pervaporation were used as the input data to perform the environmental analysis with LCA. Ecosolvent v.1.0.1 was used to calculate inventories data related to the incineration technology (waste solvent incineration and cement kiln) of the first cut of the distillation step for the case distillation/incineration and for treatment of column residues of both alternatives investigated.

Applied to the mixture isopropyl alcohol-water, optimal values for per-pass IPA recovery and distillate composition were determined for the alternative distillation/incineration and distillation/pervaporation, respectively. From the analysis of the economic figures, it was concluded that solvent recovery through the hybrid process is the better option mainly due to the savings in the cost of fresh solvent. The LCA results, performed in SimaPro 7.3, show that the main impact is related to the solvent production. Thus, solvent recovery is the best option if minimization of the use of resources is paramount. Nevertheless incineration in a cement kiln becomes relevant in terms of human health for the avoided use of fuels.

Furthermore, it was concluded that both process optimization with the aid of conceptual models and LCA are key tools in the decision-making process to determine which technology is the most appropriate for the treatment of waste solvents.

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1. Introduction

Organic solvents are widely used in the pharmaceutical industry to perform process reactions and crystallize the product. As demonstrated by Luis et al. [1], life cycle assessment (LCA) can be used as a tool to determine the best waste solvent technology

* Corresponding author at: INGAR (CONICET-UTN), Avellaneda 3657, 3000 Santa Fe, Argentina.

E-mail address: destila@santafe-conicet.gov.ar (J. Espinosa).

from an environmental point of view and even as a priori decision maker tool [2]. Issues such as the minimization of hazardous waste, emissions and, material and energy inputs are paramount in an optimal waste-solvent management [3,4].

Incineration is the more obvious option if the use of waste solvents as fuels for steam and electricity production is assessed. Waste solvent incineration and incineration in a cement kiln are alternatives that deserve attention in such a case [3,5].

Solvent recovery, on the other hand, minimizes the usage of raw materials. Batch distillation is the key recovery operation.

Nomenclature

$B1_{\alpha}$	still content at the beginning of the first cut	x_i^B	instantaneous mole fraction of component i in the still, initial value
$B1_{\omega}$	still content at the end of the first cut	x_{i0}^B	instantaneous mole fraction of component i in the still, initial value
$B2_{\alpha}$	still content at the beginning of the second cut	x_B	vector of instantaneous still compositions
$B2_{\omega}$	still content at the end of the second cut	x_D	vector of instantaneous distillate compositions
$B3_{\alpha}$	product vessel content at the beginning of the membrane operation	x_i^D	instantaneous mole fraction of component i in the distillate
$B3_{\omega}$	product vessel content at the end of the membrane operation	x_N	vector of instantaneous compositions at lower column end
D	distillate flow rate (kmol/h)	x_P	vector of instantaneous pinch compositions (II, binary; III, ternary)
F	fresh feed amount (kmol)	y_{xB}^*	vector of instantaneous vapor compositions in equilibrium with x_B
f	multiplier of the minimum reflux ratio		
M_0	still holdup (kmol)		
P_p	permeate pressure (kPa)		
R	reflux ratio		
R_{\min}	minimum reflux ratio		
t	time (h)		
t_D	distillation processing time (h)		
t_M	pervaporation processing time (h)		
V	vapor flow rate (kmol/h)		
		<i>Greek letters</i>	
		η	rectification advance
		σ_i^D	fractional recovery of component i in the distillate

However, it is noteworthy that hybrid processes comprising distillation and membrane separation technologies like pervaporation are emerging as suitable choices, mostly due to the independence of the separation performance of membrane technologies with the phase equilibrium. Hence, the hybrid process is able to break azeotropes of azeotrope forming waste streams while reducing the energy demand of the distillation task. Moreover, separations by distillation that are controlled by tangent pinch points are also candidates to be replaced by a hybrid process. Urriaga et al. [6] demonstrated the technical feasibility of isopropyl alcohol recovery with the hybrid distillation/pervaporation. Koczka et al. [7] performed economic comparisons between the state-of-the-art and hybrid alternatives in the recovery of tetrahydrofuran from binary and ternary mixtures demonstrating the economic benefits of hybrid processes including pervaporation. Slater et al. [8] proposed the integration of pervaporation with a constant volume distillation for the recovery and reuse of tetrahydrofuran. These authors assessed the effectiveness of the proposed technology resorting to an analysis taking into account both economic and environmental aspects. Applied to the mixture THF-methanol, Luis et al. [9] performed a thorough analysis of the alternatives pressure swing distillation, distillation/pervaporation and incineration in terms of their environmental impact (LCA) and energy consumption (simulation), concluding that the hybrid process can be considered a real alternative to the other technologies due to the saving in materials and energy in an overall scenario. Investment costs were not included, however, in their analysis.

In this paper, we first assessed the performance of distillation/incineration in a cement kiln and distillation/pervaporation through the conceptual design approach, to evaluate the economic figures of each alternative. Then via environmental analysis the impact of the alternatives considered in the human health, ecosystem and natural resources were estimated for the two alternatives and distinguishing two alternative incineration scenarios: waste solvent incineration and cement kiln. Quasi-optimal designs for each technological alternative are obtained resorting to conceptual models of the hybrid process [10,11]. Optimal values obtained at the conceptual design level were used as input data of the life cycle analysis to consider all impacts on humans and the environment during the entire life cycle of solvents [12,13]. To demonstrate the approach the mixture isopropyl alcohol–water, which shows both an azeotrope and an inflexion point in the vapor–liquid

diagram, is considered in this work but the methodology can be extended for any multicomponent mixture.

2. Problem statement and process description

Two process alternatives will be analyzed. For Alternative 1, the fresh feed (5 t/day with 27 wt.% IPA) is concentrated via batch distillation in order to obtain a distillate with a composition near that of the azeotrope isopropyl alcohol–water. After that, while the distillate is sent to incineration in a cement plant the column residue is diverted to biological disposal facility on-site. For Alternative 2, on the other hand, the alcohol is recovered in a two steps process comprised by a distillation column and a pervaporation unit, both units operated in a batch wise mode. As in Alternative 1, the residue of the column is sent to biological treatment and discharge. The main process specifications are: (i) The alcohol concentration in the boiler at the end of the operation should be lower than 1 wt.%, (ii) for the case of solvent recovery, the final concentration of alcohol in the product tank should be above 99.8 wt.%.

Regarding the first alternative; i.e., distillation followed by incineration “off-site” in a cement kiln, it is considered that the optimum process consists in concentrating the fresh feed to a concentration near the azeotropic composition in order to obtain a mixture with a lower calorific value above 5500 kcal/kg. In this way, support fuel is avoided. Moreover, savings are expected in haulage costs due to the decreased volume to be transported [14]. It is considered that the distillation column can operate 20 h a day, consuming the remaining 4 h for filling, starting-up and emptying the column. Main optimization variable is the “per-pass” recovery of alcohol σ_{IPA}^D in the first cut. Table 1 shows the lower calorific value corresponding to a mixture with 60 mol % (83 wt.%) of isopropyl alcohol, which is adopted as the target distillate composition during the first cut. Note that the azeotropic composition is 69.75 mol% (88.5 wt.%). The first cut is followed by a second cut operated at a constant reflux ratio (0.5) in order to achieve an IPA composition below 1 wt.% in the boiler at the end of the batch. This intermediate cut is recycled to the next batch to avoid alcohol losses, as shown in Fig. 1.

Fig. 2 shows the operating sequence corresponding to the alternative distillation/pervaporation. The sequence for the distillation column is similar to that of alternative distillation followed by

Table 1
Calorific value of the concentrated feed (Mixture 83 wt.% IPA).

Heat of combustion IPA (kcal/kg)	7201
Latent heat W (kcal/kg)	539
Lower calorific value 83% IPA	5976.83
Lower calorific value 17% W	-91.63
Lower calorific value 83:17 Mixture	6068.46

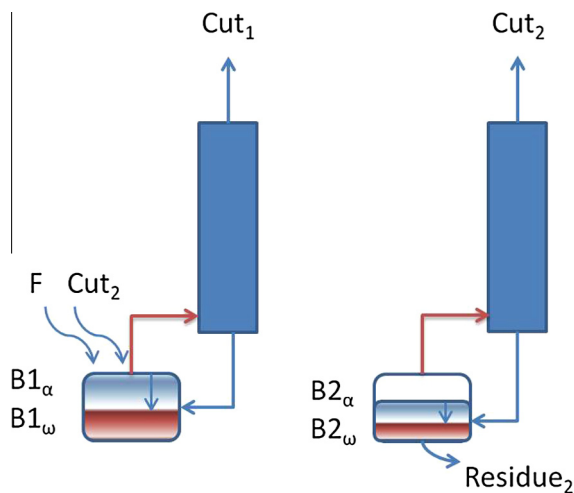


Fig. 1. Operation sequence corresponding to the alternative distillation/incineration. While the first cut is sent to the cement plant for incineration, Cut_2 is recycled to the next batch.

incineration. The first cut is sent to the membrane unit. Note that both the second cut and the permeate from the membrane unit must be recycled to the batch rectifier in the next batch to avoid IPA losses.

Obtaining a quasi-optimal design for this alternative is more complex than for the alternative distillation/incineration since values for an increased number of optimization variables must be determined. Main optimization variables are: (i) “per-pass” recovery of alcohol σ_{IPA}^D in the first cut, (ii) distillate mole fraction x_{IPA}^D in the first cut, (iii) distillation processing time t_D , (iv) pervaporation processing time t_M , and (v) permeate pressure P_P .

In order to narrow the search space it is assumed that the reflux ratio of the second cut is 0.5. The permeate pressure is 1.5 kPa [6]. Operating times for distillation and dehydration tasks are set to 16 and 20 h, respectively, according to the tasks schedule shown in Fig. 3. The cycle time is 24 h with a time-horizon of 360 days/year.

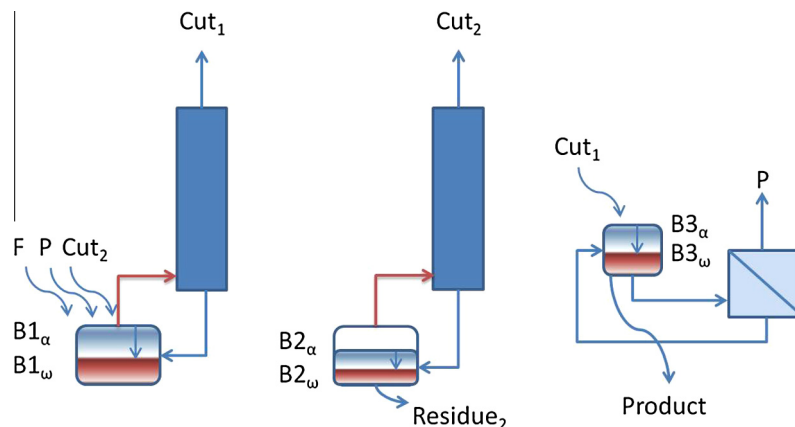


Fig. 2. Operation sequence corresponding to the alternative distillation/pervaporation.

3. Conceptual model for the batch rectifier

In this work, a quasi-optimal operation of a batch rectifier is estimated based on a conceptual model of the operation. The main assumptions of the conceptual model are (i) the rectifier has an infinite number of stages and (ii) the instant variations of the molar hold-up in the trays are negligible. Under these assumptions, the following relationships apply for every component in the mixture [15,16]:

$$\frac{d\sigma_i^D}{d\eta} = \frac{x_i^D}{x_{i0}^B} \quad (1)$$

$$x_i^B = x_{i0}^B \frac{(1 - \sigma_i^D)}{(1 - \eta)} \quad (2)$$

where σ_i^D is the fractional recovery of component i in the distillate, η is the rectification advance, x_i^D is the mole fraction of component i in the distillate, and x_{i0}^B is the initial mole fraction of component i in the still.

Eq. (1) above has the advantage of considering the component recoveries and the rectification advance instead of the component mole fractions. This choice is appropriate at the design level considering that the design specifications in batch distillation are normally given in terms of component recoveries and that the vapor flow rate does not need to be specified at this level. Note that for given instantaneous values of the rectification advance and the recovery of each component in the distillate it is possible to calculate the instantaneous still composition from Eq. (2). This equation gives the instantaneous still composition needed for calculating the instantaneous distillate composition (if the column is operated at constant reflux) or for calculating the instantaneous reflux ratio (if the column is operated at constant distillate composition).

Pinch theory allowed estimating the instantaneous rectifier performance at either constant distillate composition [17–19] or constant reflux ratio [19,20]. To this end, the geometry of the internal composition profile is approximated either by linearization of the profile in the neighborhood of pinch points or by solving the pinch equations for a limiting value of a distillate composition. The mass balance envelope used in the conceptual model is depicted in Fig. 4. Fig. 5 shows the instantaneous performance of a column separating a quaternary mixture formed by acetone, chloroform, benzene and toluene. Linearization of the internal profile in the neighborhood of the composition of the mixture in the boiler produces a plane which approximates very well the behavior of the adiabatic profile simulated in Aspen Hysys [21] and therefore, the instantaneous reflux ratio needed to achieve a given distillate

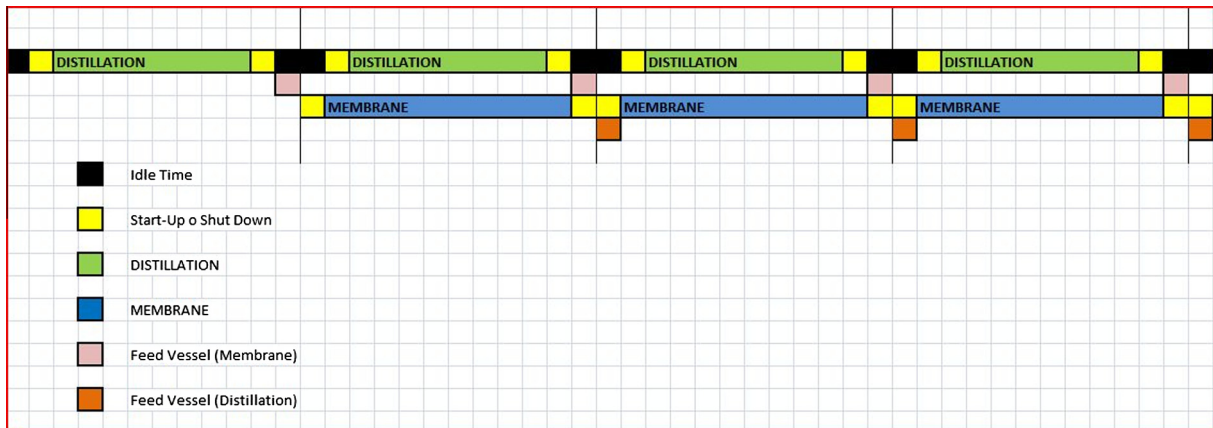


Fig. 3. "Scheduling" corresponding to the hybrid process.

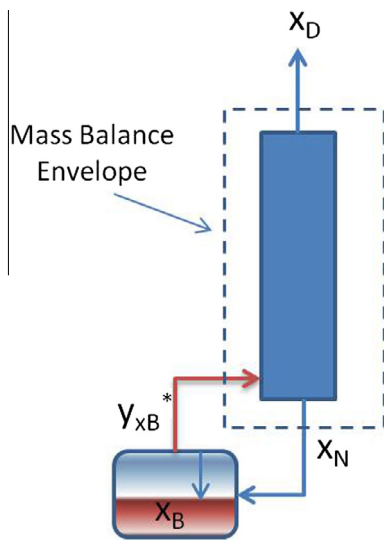


Fig. 4. Mass balance envelope used in the conceptual model of a batch rectifier.

composition. Calculation of R_{\min} is straightforward from the lever arm rule considering x_D , y_{xB}^* and x_N .

More recently, conceptual models incorporated the influence of tangent pinch points [22–24] and distillation boundaries [25–28] on both product feasibility and energy demand of highly non-ideal mixtures.

For the case under analysis, the conceptual design is characterized by the appearance of tangent pinch points. Figs. 6a–6e shows the results obtained from the integration of Eqs. (1) and (2). For the first cut, the rectification advance η was varied until achieving an alcohol "per-pass" recovery of 84%. The distillate composition was set at 60 mol% of IPA. Therefore, a variable reflux policy is calculated from pinch theory as explained by Torres and Espinosa [24]. An intermediate cut operated with a constant reflux policy (0.5) is implemented in order to achieve a water composition of 99.7 mol% in the boiler at the end of the operation. The intermediate cut is recycled to the next batch as shown in Fig. 1, in order to avoid alcohol losses. Table 2 shows the overall mole balance in pseudo-steady state, which is attained after the third batch. In this way, the aforementioned "per-pass" recovery of 84% represents an overall recovery of 97.5% of the alcohol contained in the fresh feed (5000 kg, 27 wt.% IPA) to the process. The remaining 2.5% is sent to biological treatment. Each batch processes 5450 kg with 28.8 wt.% of isopropyl alcohol.

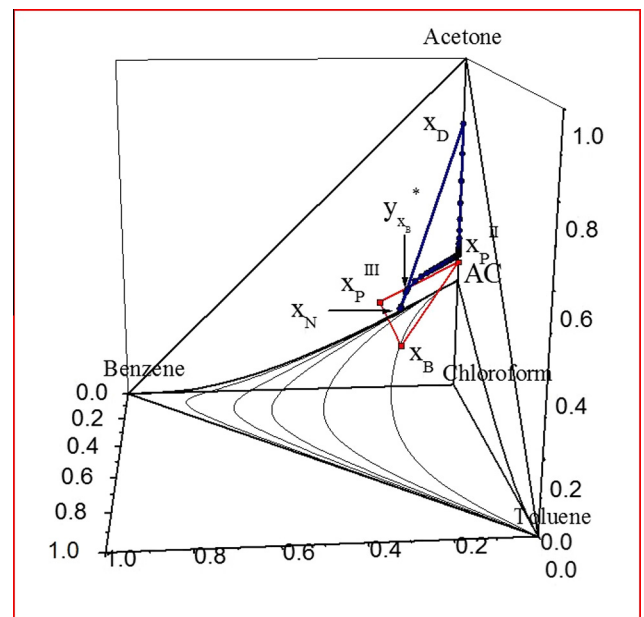


Fig. 5. Instantaneous column performance estimated with the conceptual model. The liquid profile simulated in Aspen Hysys [21] is also included. Note how the plane formed by relevant pinch points resembles appropriately the shape of the internal profile in the neighborhood of the still composition.

4. Conceptual model for the pervaporation system

As shown in Fig. 2, the membrane system is formed by a feed tank, the membrane unit itself and a recirculation pump. For the sake of simplicity, the vacuum-refrigeration system is not shown. It is worth to mention that this sub-system was optimized for each purification task (with different amounts and compositions of Cut₁ in Fig. 2) considered as explained by Sosa [11].

For the case of isopropyl alcohol dehydration with the aid of a hydrophilic membrane, the final product is obtained in the feed tank at the operation end. As long as the feed to the membrane unit increases its alcohol content with time, the driving force for separation decreases. Therefore, pervaporation modules should be arranged in parallel to maximize the driving force during the batch cycle.

In this work, the semi-empirical model based on Fick's law with concentration dependent diffusivity parameters developed by Urtiaga et al. [6] for the commercial membrane CMC-CF-23 (Celfa) was adopted. The main assumptions for the conceptual model are:

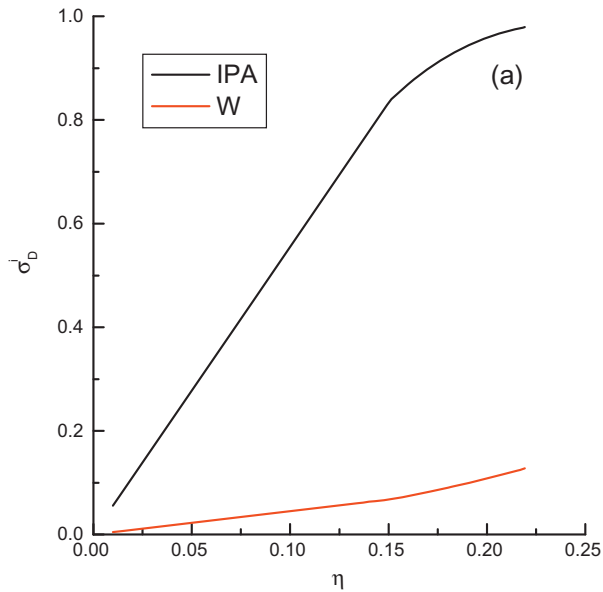


Fig. 6a. Component recovery versus rectification advance.

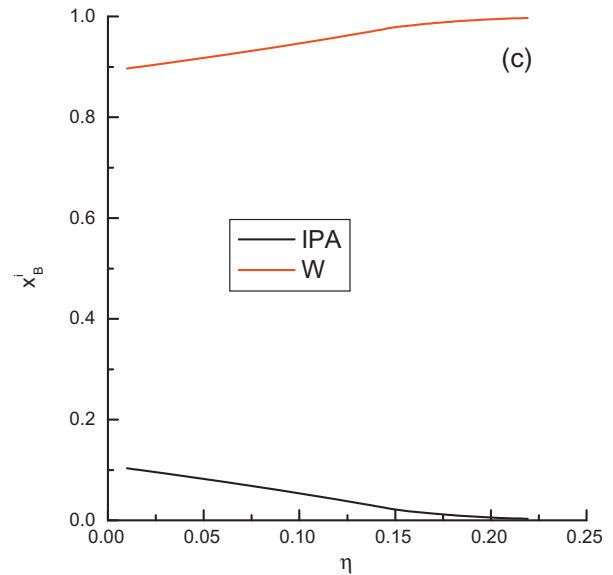


Fig. 6c. Still composition versus rectification advance.

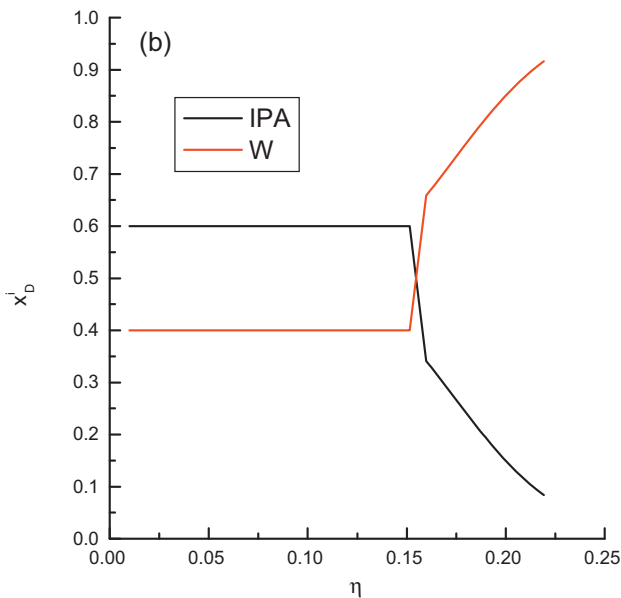


Fig. 6b. Instantaneous distillate composition versus rectification advance.

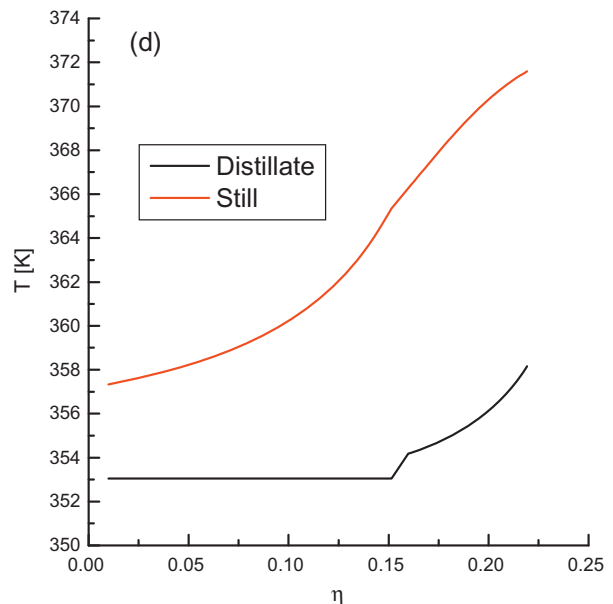


Fig. 6d. Distillate and still temperature versus rectification advance.

(i) the mass transport occurs by a solution-diffusion-desorption mechanism, (ii) pseudo steady-state of composition and temperature profiles is achieved in the membrane unit for each instant feed composition, and (iii) module geometry is not taken into account. All the mentioned assumptions, which are valid at the conceptual design level, should be removed during the detailed design step.

The model was implemented in the equation-oriented simulation software gPROMS [29]. For each alternative analyzed, the number of modules (17.5 m² each) required to achieve a final alcohol weight fraction of 0.998 is calculated. The operation time of 20 h (Fig. 3) was approximated from below but it was not exactly obeyed due to the integer nature of the solution space of the model for fixed values of the membrane area per module.

5. Optimization of alternative 1: distillation/incineration

As previously mentioned, the main optimization variable of this alternative is the IPA recovery in the first cut. At the conceptual

modeling level it is possible to establish quasi-optimal reflux policies like that shown in Fig. 6e for the case of a recovery per pass of 84%. It is noteworthy that the conceptual model of the batch rectifier decouples the variation of compositions from variation of flows and batch size. As stated by Bernot et al. [30], this kind of approach can be used to estimate batch sizes, operating times, equipment sizes, utility loads, and costs for the batch distillation. For given values of the batch size (about 5 t/batch) and operating time (20 h/batch), the only variable that must be determined is the vapor flow rate V , which can be iteratively obtained from the results obtained at the conceptual model level and the mass balance around the condenser:

$$V = \frac{1}{t_D} \int_0^{t_D} D(t)[R(t) + 1] dt = \frac{1}{t_D} \int_0^\eta M_0[R(\eta) + 1] d\eta \quad (3)$$

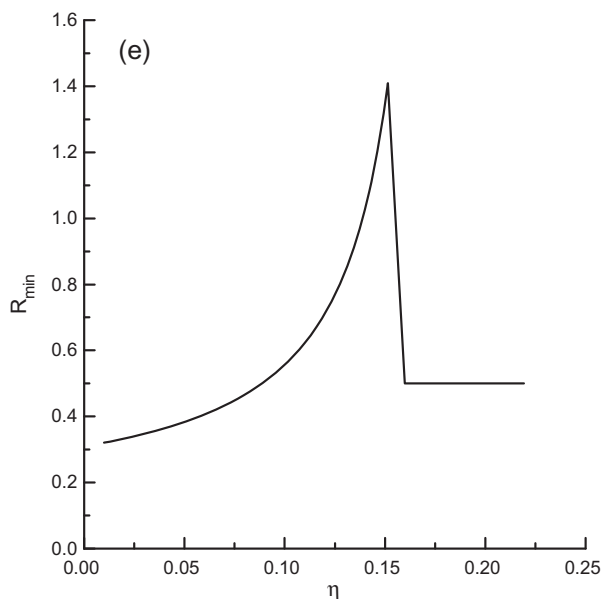


Fig. 6e. Instantaneous reflux ratio versus rectification advance.

Eq. (3) can be integrated taking into account that $D_k(t)dt$ is the product amount recovered during the time interval $[t_{k-1}, t_k]$; i.e., $D_k(t)dt = M_0(\eta_k - \eta_{k-1}) = M_0d\eta$. In Eq. (3) V is the vapor flow rate (kmol/h), D is the distillate flow rate (kmol/h), R is the instantaneous reflux ratio and M_0 is the feed amount in the boiler (kmol). For integrating Eq. (3) the instantaneous reflux ratio was calculated from:

$$R = fR_{\min} \quad (4)$$

In all studied cases the value of f was about 1.1. The number of trays was estimated with the aid of Aspen Distil [21] from $(x_B^0, R(0))$ in order to achieve the selected distillate composition x_D for the first cut at column top. The instantaneous separation at the very beginning of the operation required the greatest number of theoretical stages and hence, we adopted this criterion to estimate the value for this structural variable. The simulation of the instantaneous separation in Aspen Hysys [21] for the initial conditions was also used to determine both the column diameter and the type of internals. The tool Try Sizing (Aspen Hysys, [21]) recommended the adoption of a packing column with a diameter of 0.3048 m considering the relatively low vapor flow rates involved in all studies. The column height varied along the different designs considered.

Eq. (3) was iteratively solved for different values of V until achieving the desired value of the operation time; i.e., $t_D = 20$ h. Fig. 7 shows the values for vapor flow rates obtained for alcohol recoveries in the interval [84–98%]. The minimum value for V corresponds to a alcohol recovery “per-pass” in the first cut of around 96%.

Table 3 shows the corresponding design and operation variables. Investment and operation costs reported in Table 4 were calculated on a yearly basis (see the cost model in the Appendix Section, Supplementary Material). Among the operating costs, the costs involved in transporting the concentrated distillate (Cut₁ in

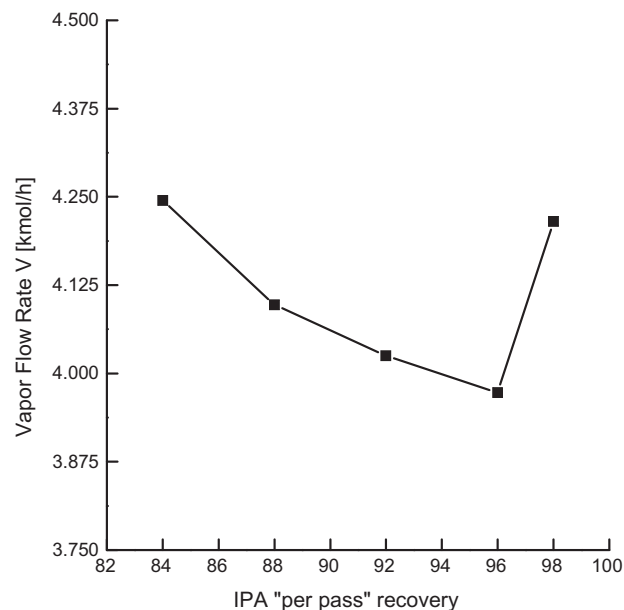


Fig. 7. Vapor flow rate for different alcohol “per-pass” recoveries in the first cut. In all cases, $t_D = 20$ h.

Table 3

Design and operation variables of the batch rectifier for different “per-pass” alcohol recovery. Alternative Distillation/Incineration.

Per pass recovery (%)	84	88	92	96	98
Condenser area (m ²)	1.839	1.775	1.744	1.721	1.826
Evaporator area (m ²)	1.402	1.353	1.329	1.312	1.392
Horizontal vessel volume (m ³)	7.9	7.7	7.5	7.3	7.2
Packed height (m)	5.0	5.0	5.0	5.0	5.0
Packed diameter (m)	0.3048	0.3048	0.3048	0.3048	0.3048
Cooling water (m ³ /year)	15212.5	14682.2	14424.1	14237.8	15105.0
Steam (kg/year)	578660.9	558486.1	548671.4	541582.9	574571.4

Fig. 1) to the cement plant were estimated from parameters given in Table 5. Twenty-nine trips with a total traveled distance of 12,760 km are required to incinerate the mixture with 83 wt.% IPA. The cost to incinerate the distillate with a lower calorific value of 6070 kcal/kg in a cement kiln is about 150 U\$/t while a cost of 650 U\$/t O₂ is assumed for the biological disposal of the column residue (Residue₂ in Fig. 1).

Consistent with the results shown in Fig. 7, the optimal recovery per batch is around 96%. However, as it is shown in Table 4, any of the design alternatives is able to be implemented since the differences in annualized costs are rather small. This result can be explained resorting to the process schedule (Fig. 3). Note that for a batch time of 20 h, a value that is sufficiently large for the separation of the given feed amount, the rectifier processing capacity measured from its cross-sectional could accommodate vapor flow rates as high as the double of the actual values. In other words, the separation could be accomplished in less time

Table 2

Overall mole balance in pseudo-steady state corresponding to an alcohol “per-pass” recovery of 84% at the end of the first cut.

	Units	Column charge	Cut ₁	Residue ₁	Cut ₂ (Recycle)	Residue ₂
Overall Amount	(kmol)	241.53	36.57	204.96	16.40	188.56
Isopropyl alcohol	(mol/mol)	0.1081	0.6000	0.0203	0.2212	0.0029
Water	(mol/mol)	0.8919	0.4000	0.9797	0.7788	0.9971

Table 4

Annualized investment and operating costs for different alcohol “per-pass” recoveries in the first cut. Alternative Distillation/Incineration.

Per pass recovery (%)	84	88	92	96	98
Column investment cost (US\$/year)	64,897	64,613	64,348	64,084	64,030
Utilities (US\$/year)	16,079	15,519	15,247	15,050	15,966
Column residue disposal (US\$/year)	19,186	19,186	19,186	19,186	19,186
Transport cost (US\$/year)	10,756	10,756	10,756	10,756	10,756
Incineration in cement kiln (US\$/year)	85,500	85,500	85,500	85,500	85,500
General Costs (US\$/year)	102,580	102,420	102,270	102,130	102,100
Overall Costs (US\$/year)	298,998	297,994	297,307	296,706	297,538
IPA to incineration (t/year)	473.8	473.8	473.8	473.8	473.8
Overall Costs (US\$/t IPA)	631	629	627.5	626.2	628

Table 5

Parameters used to calculate the transport cost [31].

Truck capacity (m ³ /trip)	25
Distance per trip (km/trip)	2 × 220
Fuel economy (km/L)	5
Fuel price (US\$/L)	0.85
Average Truck Speed (km/h)	60
Load/Unload time of products (h)	1
Driver wage (US\$/h)	10
Maintenance expenses (US\$/km)	0.0976
General expenses (US\$/d)	8.22
Truck: Purchase cost (US\$)	2E+05

maintaining the same column. The cost of 296,700 US\$/year is equivalent to a cost of 626 US\$/t IPA. Table 6 shows the mass balance in pseudo-steady state, achieved after three days, corresponding to the optimal design. The feed charge is about 5074 kg.

6. Optimization of alternative 2: distillation/pervaporation

According to the scheduling proposed in Fig. 3, different separations were simulated with operation times for distillation and purification of 16 and 20 h, respectively. The alcohol recovery per cycle was set at 92% and variants with distillate mole fractions in the range [0.6–0.675] were analyzed. The composition of the distillate is the main optimization variable if the design goal is to properly capture the cost trade-offs between the distillation column and the membrane unit.

Fig. 8 shows the vapor–liquid equilibrium diagram for IPA–water system. It is noted that the equilibrium curve of the azeotropic mixture has an inflection point **IP**, which is typical in systems where the energy demand is controlled by tangent pinch points for certain separations. In the case of starting compositions at the left of the inflection point, the choice of distillate compositions lower than x_D^{crit} will result in instantaneous separations of which the energy demand is controlled by the composition in the boiler; that is, operations with similar behavior to ideal mixtures. For distillate composition higher than x_D^{crit} , the instantaneous minimum reflux can be controlled either by a “pinch” at the bottom of the column, a tangent pinch located somewhere in the “middle” or both [24]. Note that for a composition of the distillate of 0.675 the operating line (red¹ line in Fig. 8) corresponding to the starting composition x_B^0 approaches the equilibrium curve and thus such separation requires a large number of stages.

¹ For interpretation of color in Fig. 8, the reader is referred to the web version of this article.

Fig. 9 depicts the time evolution of the main variables calculated with the conceptual model for a distillate mole fraction of 0.6. The operation cycle of the batch rectifier is 16 h with a vapor flow rate of 5.359 kmol/h. The rectifier has 13 theoretical stages and a column diameter of 0.3048 m. Table 7 shows the mass balance in pseudo-steady state corresponding to this variant. Note that the charge to the column is composed by a fresh feed, the second cut and the condensed permeate from the membrane unit (Fig. 2). The feed charge is about 5568 kg. Table 8 shows the corresponding mass balance in pseudo-steady state for the purification step in the membrane unit.

Fig. 10a and b show the simulation results of the purification step in the membrane unit corresponding to the feed charge reported in Table 8. Simulations in gPROMS [29] were done for different values of the membrane area until achieving an IPA purity equal or above 99.4 mol percent (99.8 wt.%) in an operating time equal or lower than 20 h as it is shown in the last row of Table 9. For the optimum variant the required area was 87.5 m². Modules of 17.5 m² each working in parallel were considered in order to maximize the driving force through the membrane along the batch time. Fig. 10b shows the deterioration of the driving force at the end of the batch.

Tables 9 and 10 show the optimization results. The optimal distillate mole fraction is about 0.65. At higher values of this variable there is a substantial increase in operating and investment costs of the column that does not outweigh the savings in membrane area caused by a feed (Cut₁ in Fig. 2) that is characterized by a higher alcohol composition as much as a smaller amount to be processed with respect to the rest of the designs studied. The cost of recovery for the optimal composition amounts to 860 US\$/t IPA, below the current purchase cost of IPA of 1200 US\$/t.

7. Estimation of the impact of the alternatives considered in the human health, ecosystem and natural resources

To perform the environmental analysis SimaPro 7.3 [32] was used. The goal of life cycle assessment was to evaluate the environmental impact of the two alternatives studied for one year of operation. Along with the two alternatives, solvent production and waste water treatment were included in life cycle analysis. Optimal values for the utilities, i.e., cooling water, electricity and steam needed for distillation and pervaporation were used as the input data to perform the environmental analysis with LCA [9]. Inventories corresponding to the incineration of the first cut of the distillation step in Alternative 1 and treatment of column residues in both alternatives were calculated with the aid of Ecosolvent v.1.0.1, a LCA free-software developed by Capello et al. [13,33].

For the alternative involving incineration, two different models were studied: a cement kiln [3] and a waste solvent incinerator [5]. The data inventory for these units was calculated considering a stream with the same concentration of that of Cut₁ in Table 6 but with an overall amount calculated on a yearly basis. The environmental burdens of 29 trips per year were also considered to take into account the transportation cost from the pharmaceutical factory to the incineration plant.

The environmental impact assessment was undertaken using the ReCiPe 2008 v.1.04 method from SimaPro 7.3 [32]. ReCiPe 2008 comprises two sets of impact categories with associated sets of characterization factors. Eighteen impact categories are addressed at the midpoint level [34]: (1) climate change; (2) ozone depletion; (3) terrestrial acidification; (4) freshwater eutrophication; (5) marine eutrophication; (6) human toxicity; (7) photochemical oxidant formation; (8) particulate matter formation; (9) terrestrial ecotoxicity; (10) freshwater ecotoxicity; (11) marine ecotoxicity; (12) ionising radiation; (13) agricultural land occupation;

Table 6
Mass balance in pseudo-steady state for the optimal design. Alternative Distillation/Incineration.

	Units	Column charge	Cut ₁	Residue ₁	Cut ₂ (Recycle)	Residue ₂
Overall amount	(kmol)	228.28	36.57	191.71	3.26	188.45
Isopropyl alcohol	(mol/mol)	0.1001	0.6000	0.0048	0.1077	0.0030
Water	(mol/mol)	0.8999	0.4000	0.9952	0.8923	0.9970

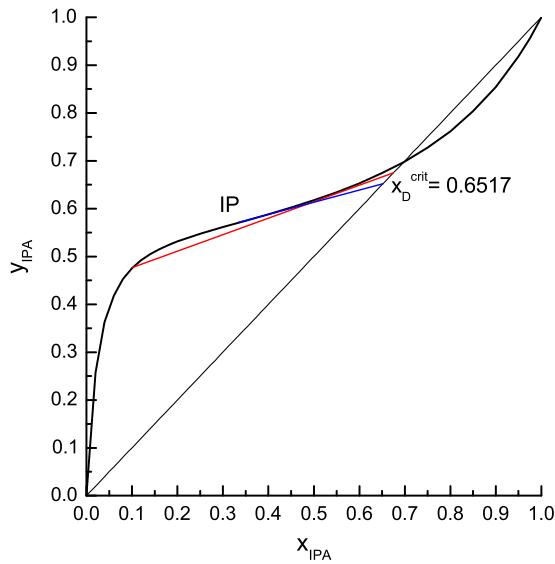


Fig. 8. Diagram y vs. x for IPA-water mixture at 101.3 kPa. **IP** represents the inflection point of the equilibrium curve.

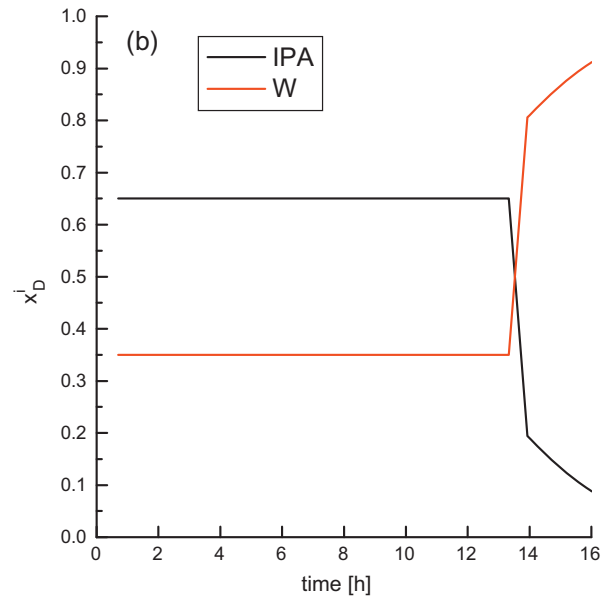


Fig. 9b. Distillate composition versus operation time. $V = 5.359$ kmol/h. $x_D = 0.65$. $\sigma_{IPA}^{Cut1} = 0.82$.

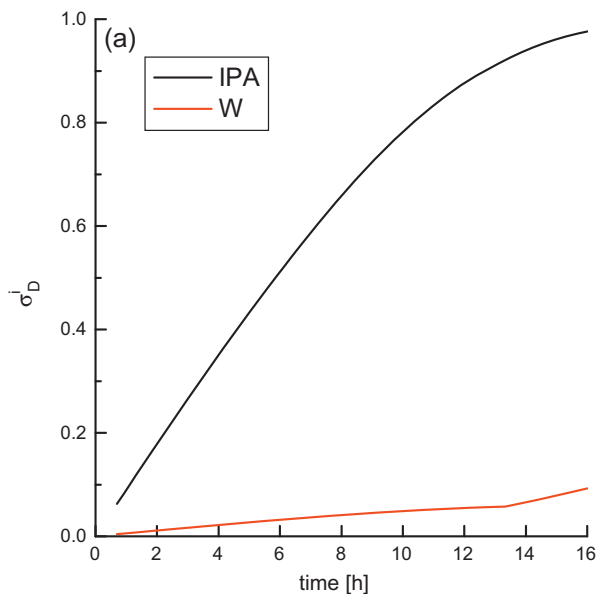


Fig. 9a. Component recovery versus operation time. $V = 5.359$ kmol/h. $x_D = 0.65$. $\sigma_{IPA}^{Cut1} = 0.82$.

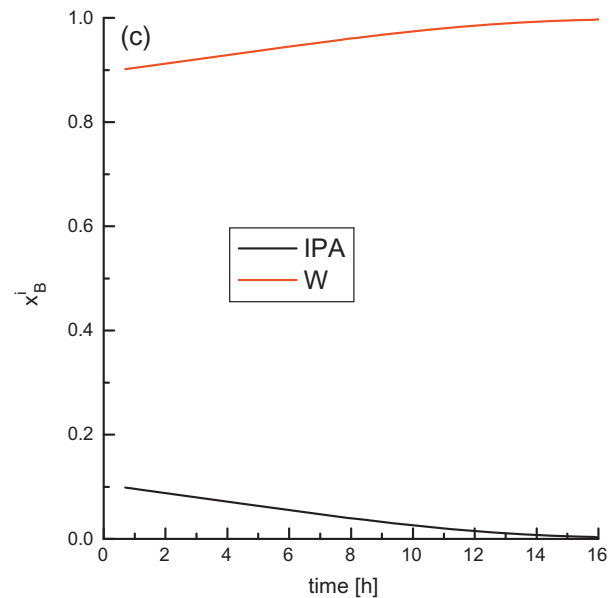


Fig. 9c. Still composition versus operation time. $V = 5.359$ kmol/h. $x_D = 0.65$. $\sigma_{IPA}^{Cut1} = 0.82$.

(14) urban land occupation; (15) natural land transformation; (16) water depletion; (17) mineral resource depletion; and (18) fossil fuel depletion. At the endpoint level, most of these midpoint impact categories are further converted and aggregated into the following three endpoint categories: (a) damage to human health, (b) damage to ecosystem diversity and, (c) damage to resource availability.

7.1. Input data for alternative 1: distillation followed by incineration of the distillate in a cement kiln

The distillate from the distillation operation (Cut₁ in Fig. 1) is incinerated off-site in a cement kiln. The column residue is sent to biological disposal. Note that both mass and energy balances

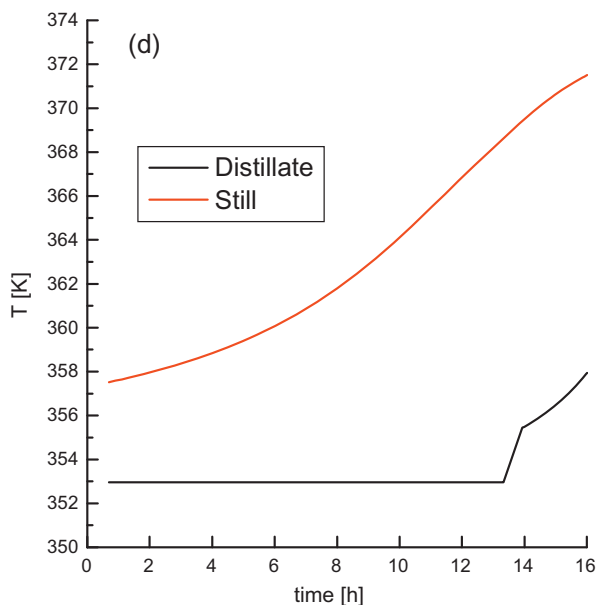


Fig. 9d. Distillate and still temperatures versus operation time. $V = 5.359$ kmol/h. $x_D = 0.65$. $\sigma_{IPA}^{Cut_1} = 0.82$.

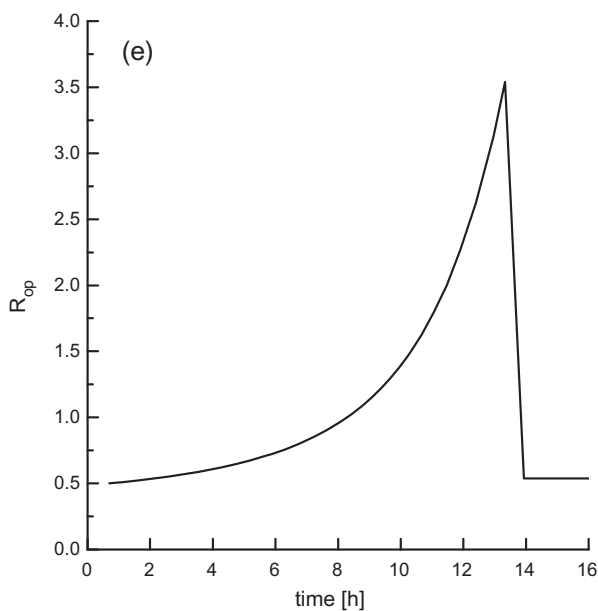


Fig. 9e. Instantaneous operating reflux ratio versus operation time. $V = 5.359$ kmol/h. $x_D = 0.65$. $\sigma_{IPA}^{Cut_1} = 0.82$.

in Table 11 are given for a batch of 20 h, one batch per day, 360 batches per year. The fuel consumption corresponding to the transport of distillate concentrate to the cement kiln is given on a yearly basis. Only 29 trips/year of a 25 m³ capacity truck are necessary.

Table 8

Mass balance in pseudo-steady state for the optimal design corresponding to the purification step in the membrane unit. Alternative Distillation/Pervaporation.

	Units	Retentate vessel Charge = Cut ₁	Product	Permeate (Recycle)
Overall amount	(kmol)	36.54	22.00	14.54
Isopropyl alcohol	(mol/mol)	0.6500	0.9949	0.1281
Water	(mol/mol)	0.3500	0.0051	0.8719

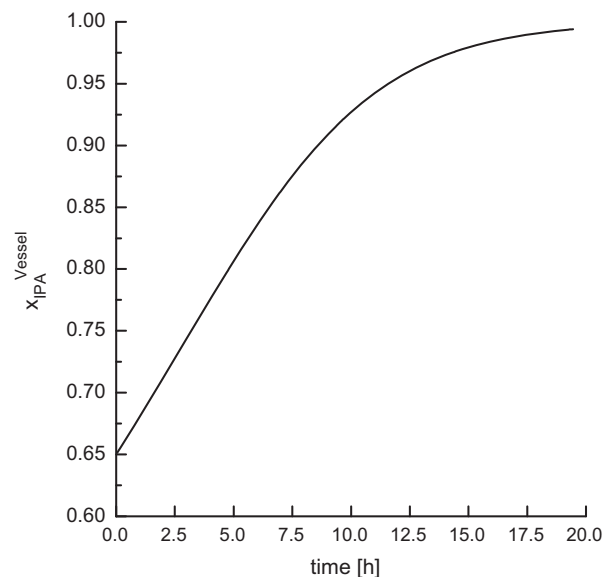


Fig. 10a. Evolution of the mole composition of isopropyl alcohol in the product tank corresponding to the optimal design. Alternative Distillation/Pervaporation.

7.2. Input data for alternative 2: distillation followed by dehydration in a pervaporation unit

The distillate from the distillation operation (Cut₁ in Fig. 2) is dehydrated on-site in a membrane unit. Note that both mass and energy balances in Table 12 are given for one batch per day, 360 batches per year.

7.3. LCA results

Figs. 11 and 12 show the environmental impact caused in the mid-points and end-points, respectively. The first column in these figures shows the results for the alternative distillation/pervaporation. The same is shown for the alternative distillation/incineration in a cement kiln in the third column. The second column refers to the alternative distillation/waste solvent incineration.

The results show that Alternative 1-waste solvent incineration, which uses a conventional incinerator, generates the largest impact. Alternative 1 with incineration in a cement kiln shows an environmental burden for resources depletion while it brings benefits for end-points human health and ecosystem quality. On the other hand, the alternative distillation/pervaporation, does

Table 7

Mass balance in pseudo-steady state for the optimal design corresponding to the distillation step. Alternative Distillation/Pervaporation.

	Units	Column charge	Cut ₁	Residue ₁	Cut ₂ (Recycle)	Residue ₂
Overall amount	(kmol)	248.77	36.54	212.22	9.34	202.88
Isopropyl alcohol	(mol/mol)	0.1038	0.6500	0.0097	0.1543	0.0030
Water	(mol/mol)	0.8962	0.3500	0.9903	0.8457	0.9970

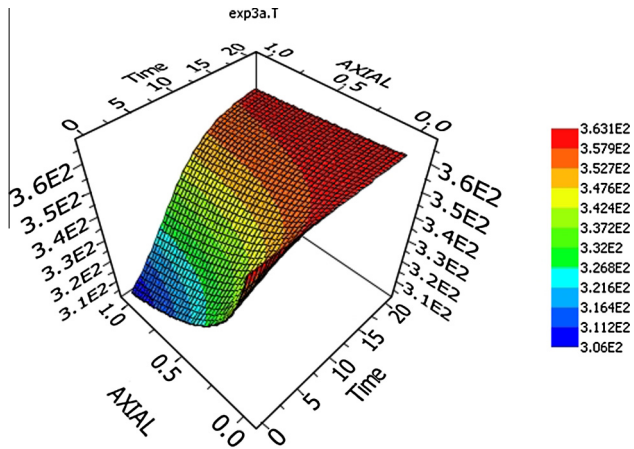


Fig. 10b. Evolution of the temperature along the retentate side of the membrane unit. Maximum operation temperature was set to 90 °C.

Table 9

Design and operation variables for different values of the distillate composition of the first cut. Alternative Distillation/Pervaporation.

Distillate composition	0.6	0.625	0.65	0.675
<i>Column</i>				
Condenser area (m ²)	2.351	2.355	1.693	1.645
Evaporator area (m ²)	1.792	1.795	1.290	1.254
Horizontal vessel volume (m ³)	7.36	7.36	7.36	7.36
Packed height (m)	5.0	5.5	8.0	14.0
Packed diameter (m)	0.3048	0.3048	0.3048	0.3048
Cooling water (m ³ /year)	15,556	15,582	15,364	16,473
Steam (kg/year)	591,720	592,701	584,413	626,616
Operating time, t _D (h)	20	20	20	20
<i>Membrane unit</i>				
Vessel (m ³)	3	2.95	2.9	2.86
Vacuum pump duty (kW)	1.60	1.59	1.46	1.44
Compressor duty (kW)	7.75	7.50	6.03	6.80
Permeate condenser area (m ²)	8.4	8.1	6.5	6.2
Retentate heater area (m ²)	1.05	1.01	0.81	0.77
Propane condenser area (m ²)	4.4	4.2	3.4	3.2
Membrane area (m ²)	105	105	87.5	87.5
Vacuum vessel volume (m ³)	5.3	5.3	4.7	4.7
Cooling water (m ³ /year)	17,776	16,568	14,851	13,678
Steam (kg/year)	136,577	124,887	112,790	101,700
Energy consumption (kW h/year)	37,846	35,056	33,529	30,828
Operating time, t _M (h)	17.65	16.9	19.45	18.65

Table 10

Annualized investment and operating costs for different values of the distillate mole fraction of the first cut. Alternative Distillation/Pervaporation.

Distillate composition	0.6	0.625	0.65	0.675
Pervaporation unit investment cost (US\$/year)	126,678	125,938	113,874	113,139
Column investment cost (US\$/year)	64,585	66,070	72,674	87,271
Column utilities (US\$/year)	16,442	16,470	16,239	17,412
Column residue disposal (US\$/year)	19,188	19,188	19,188	19,188
Pervaporation unit utilities (US\$/year)	5084	4677	4214	3826
Pervaporation unit electricity (US\$/year)	4640	4298	4110	3779
IPA loss (vacuum pump) (US\$/year)	1469	1383	1270	1184
Membrane replacement (US\$/year)	5308	5308	4423	4423
General costs (US\$/year)	173,077	173,493	170,448	178,181
Overall costs (US\$/year)	416,471	416,825	406,440	428,403
IPA recovered (t/year)	473	473	473	473
Overall recovery costs (US\$/t IPA)	880	881	859	906

not show any benefits, although its burden, in particular for resources is rather small whether it is compared with the other two.

Table 11

Input data for LCA. Alternative Distillation/Incineration.

Mass balance per batch, one batch of 20 h per day, 360 batches/year			
	Feed	Distillate	Residue
Overall amount (kg/batch)	5000	1582.2	3417.8
Isopropyl alcohol (mass fraction)	0.27	0.8334	0.0092
Water (mass fraction)	0.73	0.1666	0.9908
Energy balance per batch, one batch of 20 h per day, 360 batches/year			
Steam at 2 bar (kg/batch)	1504.4		
Cooling water (m ³ /batch)	39.5		
Transport of distillate from Pharmaceutical Company to Cement kiln			
Number of trips/year	29		
Distance/trip (km/trip)	440		
Fuel economy (km/L)	5		
Fuel consumption (L)	2552		

Table 12

Input data for LCA. Alternative Distillation/Pervaporation.

Mass balance per batch, one batch per day, 360 batches/year			
	Feed	Product	Residue
Overall amount (kg/batch)	5000	1317.4	3682.6
Isopropyl alcohol (mass fraction)	0.27	0.9985	0.0094
Water (mass fraction)	0.73	0.0015	0.9906
Energy balance per batch, one batch per day, 360 batches/year			
<i>Distillation column (18 h/batch)</i>			
Steam at 2 bar (kg/batch)		1623.4	
Cooling water (m ³ /batch)		42.7	
<i>Membrane unit (19.45 h/batch)</i>			
Steam at 2 bar (kg/batch)		313.3	
Cooling water (m ³ /batch)		41.3	
Compressor electricity consumption (kW h/batch)		66.8	
Vacuum pump electricity consumption (kW h/batch)		25.1	
Circulating pump electricity consumption (kW h/batch)		1.2	

By analyzing Fig. 11, the impact on the resources is related to the fossil depletion (kg eq. of oil). This is due to the impact of using energy during solvent production. It is noteworthy that for alternative 2, the environmental burden corresponding to this category is very low if compared with the others, since in this case almost all the isopropanol in the feed is recovered. Thus the only impact for alternative distillation/membrane is due to the utilities used to purify the feed. For Alternative 1-waste solvent incineration, fossil depletion is higher than in the case of incineration with a cement kiln, because further energy is needed to burn the solvent.

However for the two incineration cases, the clear difference in results can be found in the categories: climate change, human health and particulate formation. In fact, for the alternative distillation/incineration in a cement kiln a positive effect to the environment is expected because heavy fuel, hard coal and their corresponding emissions are avoided.

In terms of the decision-making process, if the designer is interested in minimizing the use of resources, then alternative 2 is the best choice, even when it produces a small impact in terms of human health and ecosystem quality. The importance of the impact associated to solvent manufacture was noticed in some previous works [1,2], confirming the importance of using and developing solvent recovery technologies. On the other hand, when ecosystem quality and in particular human health are paramount, alternative 1 with incineration in a cement kiln plant is the better choice.

8. Conclusions

Applied to the mixture isopropyl alcohol-water, quasi-optimal designs for the alternative distillation/incineration and

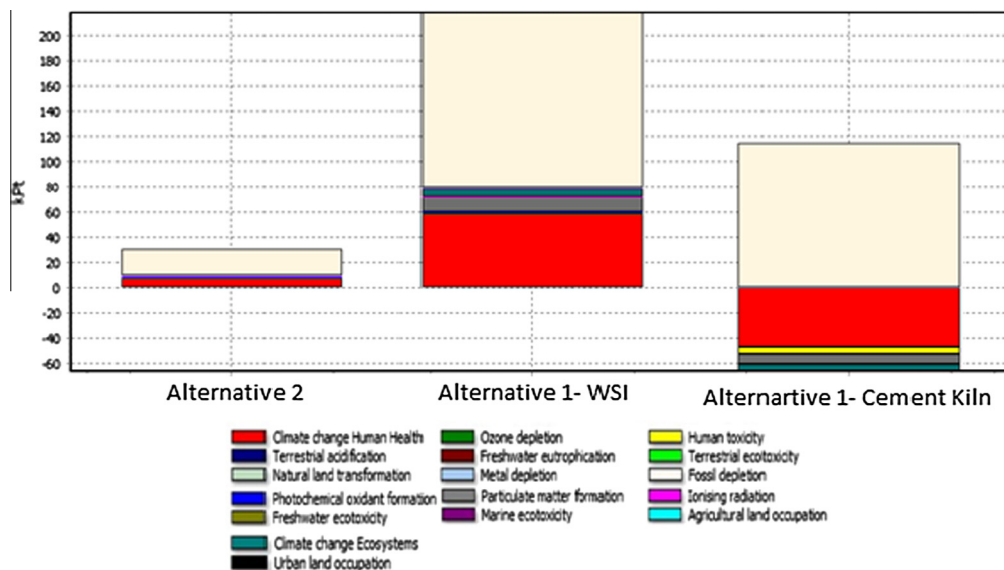


Fig. 11. Environmental impact (ReCiPe) caused in different impact categories (mid-points) when distillation/pervaporation (first column), distillation/incineration in a cement kiln (third column) and distillation/WSI (second column) are considered.

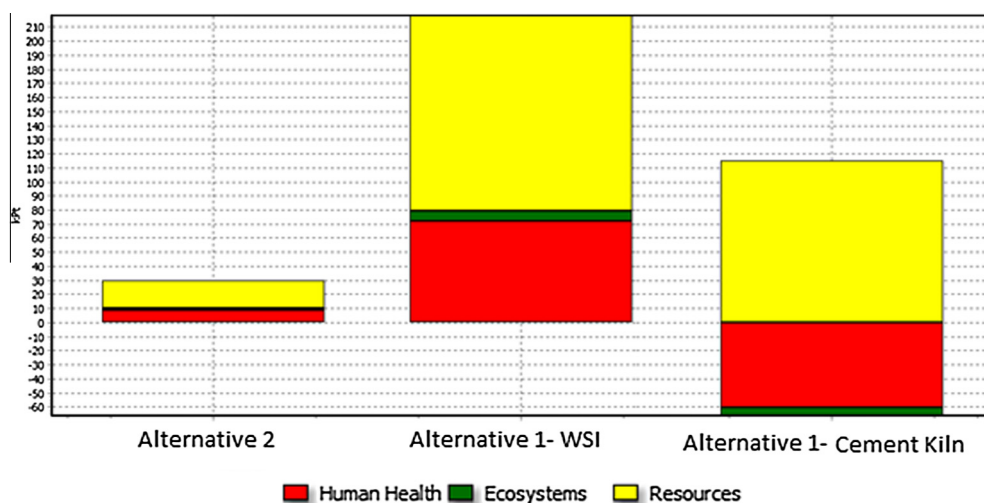


Fig. 12. Environmental impact (ReCiPe) caused in different impact categories (end-points) when distillation/pervaporation (first column), distillation/incineration in a cement kiln (third column) and distillation/WSI (second column) are considered.

distillation/pervaporation were obtained from the conceptual design of the two waste solvent technologies. The main advantage of the conceptual design approach is that process trade-offs are properly captured. Indeed, pseudo-steady state solutions, which are normally neglected when the process is modeled by rigorous simulation, are easily handled in the conceptual modeling framework. Optimal values for per-pass IPA recovery and distillate composition were determined for the first and second alternative, respectively. From the analysis of the economic figures, it is concluded that solvent recovery through the hybrid process is the better option mainly due to the savings in the purchase of fresh solvent.

The analysis was complemented by a life cycle assessment, with input data from the conceptual design step, as a tool to determine which technology is the most appropriate for the treatment of waste solvents from an environmental point of view. In this work, it was observed that the main impact is caused during the solvent

production. Solvent recovery showed the lowest values in terms of total score and it is the best option if minimization of the use of resources is paramount; on the other hand when only human health is considered, cement kiln is better.

Regarding the performance assessment approach, it was concluded that life cycle analysis is enriched by input data obtained from the conceptual model-based process optimization of each alternative studied especially in terms of process knowledge and reliability of results.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2015.12.024>.

References

- [1] P. Luis, A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen, Life cycle assessment of alternatives for waste-solvent valorization: batch and continuous distillation vs incineration, *Int. J. Life Cycle Assess.* 18 (2013) 1048–1061.
- [2] A. Amelio, G. Giuseppe, S. Vreysen, P. Luis, B. Van der Bruggen, Guidelines based on life cycle assessment for solvent selection during the process design and evaluation of treatment alternatives, *Green Chem.* 16 (2014) 3045–3063.
- [3] C. Seyler, S. Hellweg, M. Monteil, K. Hungerbühler, Life cycle inventory for use of waste solvent as fuel substitute in the cement industry: a multi-input allocation model, *Int. J. Life Cycle Assess.* 10 (2) (2004) 120–130.
- [4] C. Seyler, C. Capello, S. Hellweg, C. Bruder, D. Bayne, A. Huwiler, K. Hungerbühler, Waste-solvent management as an element of green chemistry: a comprehensive study on the Swiss chemical industry, *Ind. Eng. Chem. Res.* 45 (2006) 7700–7709.
- [5] C. Seyler, T.B. Hofstetter, K. Hungerbühler, Life cycle inventory for thermal treatment of waste solvent from chemical industry: a multi-input allocation model, *J. Clean Prod.* 13 (2005) 1211–1224.
- [6] A.M. Urriaga, E.D. Gorri, I. Ortiz, Pervaporative recovery of isopropanol from industrial effluents, *Sep. Purif. Technol.* 49 (2006) 245–252.
- [7] K. Koczka, J. Manczinger, P. Mizsey, Z. Fonyo, Novel hybrid separation processes based on pervaporation for THF recovery, *Chem. Eng. Process.* 46 (2007) 239–246.
- [8] C.S. Slater, M.J. Savelski, T.M. Moroz, M.J. Raymond, Pervaporation as a green drying process for tetrahydrofuran recovery in pharmaceutical synthesis, *Green Chem. Lett. Rev.* 5 (1) (2012) 55–64.
- [9] P. Luis, A. Amelio, S. Vreysen, V. Calabro, B. Van der Bruggen, Simulation and environmental evaluation of process design: distillation vs. hybrid distillation–pervaporation for methanol/tetrahydrofuran separation, *Appl. Energy* 113 (2014) 565–575.
- [10] M. Skiborowski, A. Harwardt, W. Marquardt, Conceptual design of distillation based hybrid separation processes, *Annu. Rev. Chem. Biomol. Eng.* 4 (2013) 45–68.
- [11] M.A. Sosa, D.A. Figueroa Paredes, J.C. Basílico, B. Van der Bruggen, J. Espinosa, Screening of pervaporation membranes with the aid of Conceptual Models: an application to bioethanol production, *Sep. Purif. Technol.* 146 (2015) 326–341.
- [12] T.B. Hofstetter, C. Capello, K. Hungerbühler, Environmentally preferable treatment options for industrial waste solvent management, a case study of a toluene containing waste solvent, *Process Saf. Environ.* 81 (3) (2003) 189–202.
- [13] C. Capello, S. Hellweg, B. Badertscher, H. Betschart, K. Hungerbühler, Environmental assessment of waste-solvent treatment options, Part I: The Ecosolvent tool, *J. Ind. Ecol.* 11 (4) (2007) 26–38.
- [14] I.M. Smallwood, *Solvent Recovery Handbook*, McGraw-Hill, New York, 1993.
- [15] H.E. Salomone, O.J. Chiotti, O.A. Iribarren, Short-cut design procedure for batch distillations, *Ind. Eng. Chem. Res.* 36 (1) (1997) 130–136.
- [16] J. Espinosa, J.L. Marchetti, Conceptual modeling and referential control applied to batch distillations, *Ind. Eng. Chem. Res.* 46 (2007) 6000–6009.
- [17] H. Offers, R. Duessel, J. Stichlmair, Minimum energy requirements of distillation processes, *Comput. Chem. Eng.* 19 (Suppl) (1995) S247–S252.
- [18] S. Brueggemann, J. Oldenburg, W. Marquardt, Combining conceptual and detailed methods for batch distillation process design, in: C.A. Floudas, R. Agrawal (Eds.), *Proceedings of FOCAPD*, Elsevier, New York, 2004, pp. 247–250.
- [19] J. Espinosa, S. Brueggemann, W. Marquardt, Application of the rectification body method to batch rectification, in: L. Puigjaner, A. Espuña (Eds.), *ESCAPE-15*, Elsevier, New York, 2005, p. 757.
- [20] J. Espinosa, E. Salomone, Minimum reflux for batch distillations of ideal and nonideal mixtures at constant reflux, *Ind. Eng. Chem. Res.* 38 (1999) 2732.
- [21] Aspen Distil & Aspen Hysys Version 8 User Manual, 2014.
- [22] A. Lucia, A. Amale, R. Taylor, Distillation pinch points and more, *Comput. Chem. Eng.* 32 (2008) 1342–1364.
- [23] K.A. Torres, J. Espinosa, Incorporating tangent pinch points into the conceptual modeling of batch distillations: Ternary mixtures, *Ind. Eng. Chem. Res.* 48 (2) (2009) 857–869.
- [24] K.A. Torres, J. Espinosa, The influence of tangent pinch points on the energy demand of batch distillations: development of a conceptual model for binary mixtures, *Ind. Eng. Chem. Res.* 50 (2011) 6260–6275.
- [25] L.J. Krolikowski, Determination of distillation regions for non-ideal ternary mixtures, *AIChE J.* 52 (2005) 532.
- [26] S. Brueggemann, W. Marquardt, Conceptual design of distillation processes for mixtures with distillation boundaries: I. Computational assessment of split feasibility, *AIChE J.* 6 (2011) 1526.
- [27] S. Brueggemann, W. Marquardt, Conceptual design of distillation processes for mixtures with distillation boundaries: II. Optimization of recycle policies, *AIChE J.* 6 (2011) 1540.
- [28] K.A. Torres, J. Espinosa, Incorporating pinch distillation boundaries into the conceptual modeling of batch distillations: Ternary mixtures, *Ind. Eng. Chem. Res.* 51 (2012) 15448–15455.
- [29] gPROMS User Manual, Process Systems Enterprise Ltd., 1998.
- [30] C. Bernot, M.F. Doherty, M.F. Malone, Design and operating targets for nonideal multicomponent batch distillation, *Ind. Eng. Chem. Res.* 32 (1993) 293–301.
- [31] F.D. Mele, A.M. Kostin, G. Guillén-Gosálbez, L. Jiménez, Multiobjective model for more sustainable fuel supply chains. A case study of the sugar cane industry in Argentina, *Ind. Eng. Chem. Res.* 50 (2011) 4939–4958.
- [32] PréConsultants, 2001, *SimaPro*, 5th edition (Amersfoort).
- [33] C. Capello, S. Hellweg, K. Hungerbühler, Environmental assessment of waste-solvent treatment options, Part II: General rules of thumb and specific recommendations, *J. Ind. Ecol.* 12 (1) (2008) 111–127.
- [34] M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs, R. van Zelm, *ReCiPe 2008: a life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level*, Report I: Characterisation, 1st ed., 6 January 2009.