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## Conceptual model-based design and environmental evaluation of waste solvent technologies: Application to the separation of the mixture acetone-water

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### ABSTRACT

In this paper, two waste solvent technologies are presented as alternatives to the disposal of spent acetone-water mixtures.

In the first alternative, a batch rectifier is used to concentrate the waste in order to obtain a distillate with a higher calorific value, which is then sent to off-site incineration either in a cement kiln or in a conventional waste solvent incinerator. The second alternative is a hybrid process composed by a batch rectifier and a pervaporation unit that processes in batchwise mode the first cut from the distillation task to obtain a dehydrated solvent. Here, four scenarios are considered, comprising two kinds of membrane materials and two different vacuum systems.

For each alternative, the conceptual design was carried out with the aid of conceptual models of the unit operations involved. Quasi-optimal values for design and operation variables were used as input data to perform an economical and an environmental assessment of each alternative. The economic analysis suggests that the hybrid process is the best alternative given that the replacement cost of fresh solvent (about 850 U\$/ton) is considered as a credit value.

From the environmental analysis with life cycle assessment, two main conclusions can be drawn: i) the use of the distillate as an alternative fuel in a cement kiln leads to a reduction in emissions that is relevant for the categories related to human health and ecosystem quality; and ii) in terms of resource depletion, the hybrid process distillation/pervaporation with the ceramic membrane HybSi (Pervatech) shows the lowest impact due to the solvent recovery.

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assessment

## Introduction

Acetone is widely used in the production of explosives, plastics, rubber, fibers, leather, oil, and paint and is a very important solvent in the pharmaceutical industry,<sup>[1]</sup> particularly for the production of methylmetacrylate and bisphenol.<sup>[2,3]</sup> The global consumption of acetone is around six million tons per year<sup>[2]</sup> and its overall demand is rising annually.<sup>[3,4]</sup> The production of acetone is carried out via oxidation of cumene or propene, or alternatively by dehydrogenation of 2-propanol.

Acetone does not form an azeotrope with water but it is difficult to separate by simple distillation from mixtures with low water concentration,<sup>[5]</sup> requiring a large amount of energy due to the presence of a tangent pinch point.<sup>[1,6]</sup> The appearance of tangent pinch points in highly non-ideal mixtures is related to the existence of an inflection point in the  $y$ - $x$  phase diagram, which in turn is generated from an

inflection in the isobaric  $T$ - $x$ - $y$  curve.<sup>[7]</sup> Calculation methods to find the minimum energy demand were developed by several authors for continuous distillation<sup>[8,9]</sup> and even for the batchwise operation mode.<sup>[10,11]</sup> Because of the ease of stripping acetone from water and the comparative difficulty of producing a dry distillate, acetone is particularly well suited to be recovered in a batch rectifier rather than in a continuous fractionating column.<sup>[12]</sup>

Other separation techniques have been thoroughly investigated for the acetone-water mixture. Some authors<sup>[13,14]</sup> showed the possibility to apply vapor permeation to recover acetone from water. Another study coupled absorption and pervaporation to recover acetone from air.<sup>[15]</sup> The separation via pervaporation was also considered.<sup>[5,16–18]</sup> Hydrophobic membranes were applied to purify the water stream for the production of pure acetone.<sup>[19,20]</sup> Nevertheless, the main application is the dehydration of acetone stripped with water.<sup>[21]</sup> Chapman

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et al.<sup>[6]</sup> investigated the possibility to remove water from acetone via pervaporation after a previous distillation concentration step. This work<sup>[6]</sup> shows that the separation of this mixture can be successfully achieved in different ways but if a high product purity is considered a hybrid process could be a suitable way.

Life cycle assessment (LCA) is commonly applied to evaluate the impacts of products and processes on the environment.<sup>[22–24]</sup> For the case of waste solvent technologies, LCA can be used as a tool to assess the best technology from an environmental standpoint. Minimization of hazardous wastes, emissions, material, and energy is of paramount importance in an optimal waste-solvent management.<sup>[25–27]</sup>

This work considers different new solutions to treat a mixture acetone-water, resulting from the pharmaceutical industry, as alternatives to the usual disposal off-site in a solvent incineration plant.

In the first alternative, the waste is processed in a batch rectifier in order to obtain a distillate with a high calorific value, which is then sent to off-site incineration either in a cement kiln or in a conventional waste solvent incinerator (WSI).

In the second alternative, on the other hand, a hybrid process composed by a batch rectifier and a pervaporation unit is considered. The main distillate stream obtained in the rectification task is processed in batchwise mode in a pervaporation unit to obtain a dehydrated solvent. In this case, the dehydrated acetone is recycled to the main pharmaceutical process thus minimizing the use of fresh solvent. Here, four scenarios are considered, comprising two kinds of membrane materials and two different vacuum systems.

For each waste solvent treatment technology considered in this work, the corresponding conceptual design is first carried out by means of shortcuts or conceptual models of the unit operations involved.<sup>[24,28]</sup> For the case of the distillation task, results are refined through rigorous simulation in Aspen Batch Distillation<sup>[29]</sup> to take into account the hold-up issue.<sup>[30]</sup> Then, an economic analysis is assessed by estimating both investment and operation costs.<sup>[24,31–35]</sup> Finally, in order to get a wider assessment, an environmental analysis with LCA is performed.<sup>[24,31,33–37]</sup> To this end, the software SimaPro 7.3<sup>[38]</sup> was used.

## Materials and methods

In this work, two membrane materials are considered: a ceramic membrane from Pervatech (HybSi) and a polymeric one reported in the work of Ray & Ray.<sup>[17]</sup> Experimental data in the range of interest (0–5 wt. % water) are available. The HybSi membrane was studied at 120°C with an initial concentration of 20 wt. % water; the

**Table 1.** Comparison of dehydration performance of the membranes considered in this work at 10 wt. % water in feed.

Membrane	Operating temperature (K)	Overall flux (kg/(m <sup>2</sup> h))	Separation factor $\frac{y_p/(1-y_p)}{x_p/(1-x_p)}$	PSI (kg/(m <sup>2</sup> h))
HybSi (Pervatech)	393.15	14.1	891	12560
Polymeric <sup>[17]</sup>	303.15	0.34	5.4	1.84

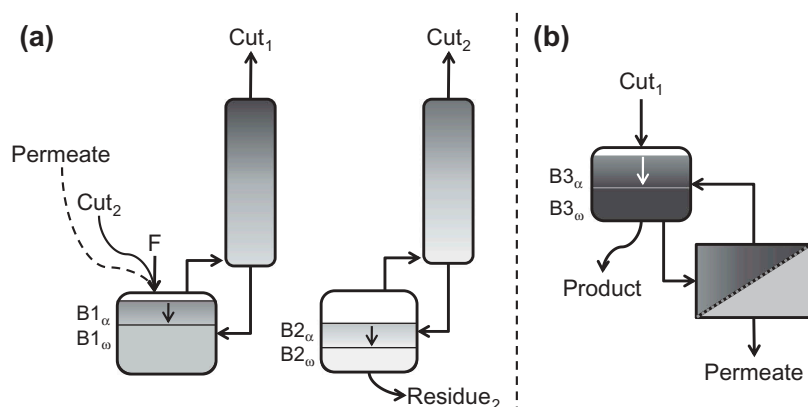
data were furnished by the company. The data for the polymeric membrane were obtained from the mentioned paper<sup>[17]</sup> and correspond to experiments at 30°C in the range 0–100 wt. % water. For the considered membranes, Table 1 shows flux and selectivity data together with the pervaporation separation index (PSI) at 10 wt. % water in feed. It is noteworthy that the separation factor for the ceramic membrane remains high even for water mass fractions in feed as low as 0.01.

## Problem statement and process description

Two main process alternatives were analyzed according to Figure 1(a)–(b). In both alternatives, a fresh feed (2.2 t/day, 58 wt. % acetone) is concentrated via batch distillation in order to obtain an acetone-rich distillate. The acetone concentration in the boiler at the end of the operation should achieve an adequate value to be diverted to an on-site biological disposal facility. It is considered that the distillation column can operate 6 hours (first shift) per day, using the remaining 2 hours for filling, starting-up and emptying the column. The first cut (Cut<sub>1</sub>) is followed by a second cut (Cut<sub>2</sub>) operated at a constant reflux ratio (0.5) in order to achieve an acetone composition below 1 wt. % in the boiler at the end of the batch.

In Alternative 1, the first cut is sent to off-site incineration either in a cement kiln or in a conventional WSI. The second cut is recycled to the next batch. On the other hand, in Alternative 2 the first cut is sent to a pervaporation unit, which is also operated in a batchwise mode during the second shift (6 hours). The acetone-rich distillate is concentrated in the product tank at a composition above 99 wt. %. In this case, the dehydrated acetone is able to be recycled to the main pharmaceutical process thus minimizing the use of fresh solvent. Note that both the second cut of the distillation task and the permeate from the membrane unit must be recycled to the batch rectifier in the next batch to avoid acetone losses.

Regarding the first alternative, that is, distillation followed by off-site incineration either in a cement kiln or in a WSI, it is considered that the optimum process consists in concentrating the fresh feed to a concentration value leading to a mixture with a lower calorific value above 23 MJ/kg. Table 2 shows the lower calorific value corresponding to a mixture with 85 mol % (94.8 wt. %) of



**Figure 1.** Operation sequence corresponding to: (a) Alternative 1, the first cut is sent to off-site incineration, while the second cut is recycled to the next batch, (b) Alternative 2, the first cut is treated in the pervaporation unit while both the second cut and the permeate of the membrane unit are recycled to the batch rectifier in the next batch.

**Table 2.** Lower calorific value (MJ/kg) of the concentrated feed (Mixture 95 wt. % acetone).

Heat of combustion A	28.5
Latent heat W	2.3
Lower calorific value 94.8% A	27.0
Lower calorific value 5.2% W	-0.1
Lower calorific value 95:5 mixture	26.9

acetone, which is adopted as the target distillate composition during the first cut. In this way, support fuel is avoided and savings in haulage costs are expected due to the decreased volume to be transported.<sup>[12]</sup>

Operating times for distillation and dehydration tasks are set to 6 hours each according to the tasks schedule shown in Figure 2. The cycle time is 16 hours with a time-horizon of 360 days/year.

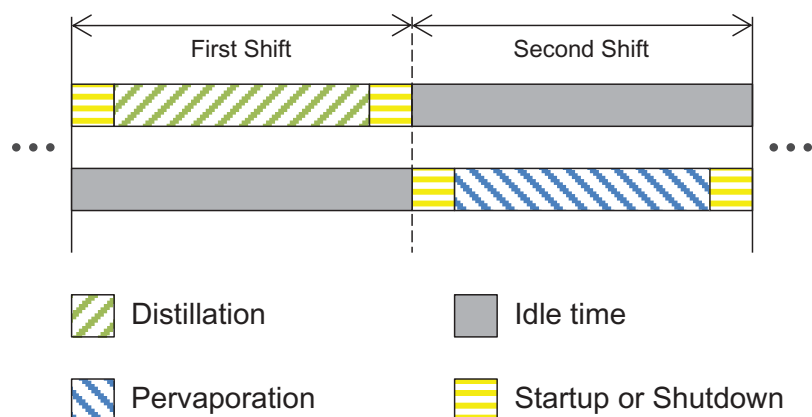
Table 3 summarizes the different scenarios considered in this work. Note that while Alternatives A21 and A23 use a vacuum pump/refrigeration system as condensation technology for vacuum production on the permeate side; in Alternatives A22 and A24 a steam-jet ejector system is adopted. In the last two cases, the water-rich liquid permeate stream leaving the ejector is merged with the residue of the column obtained at operation end in the

previous batch and sent to biological treatment and discharge.

Based on limiting operating conditions for the distillation and membrane tasks operated in batch mode, the quasi-optimal reflux ratio profile<sup>[11]</sup> and the minimum area requirement can be properly estimated. A simple algorithm is proposed to calculate the minimum area needed for a given separation in a pervaporation membrane. The environmental impacts from the entire life cycle of the solvents comparing the two technologies were assessed using the software SimaPro 7.3.<sup>[38]</sup>

### Conceptual model for the distillation task

A quasi-optimal operation of the batch rectifier is estimated based on a conceptual model of the operation. The conceptual model adopted in this paper, which is written in terms of the fractional recoveries of the mixture components in the distillate  $\sigma_i^D$  and the rectification advance  $\eta$ , is thoroughly explained by Torres & Espinosa<sup>[11]</sup> for binary mixtures showing tangent pinch points. Like in the mentioned contribution, the case-study analyzed in this paper is



**Figure 2.** "Scheduling" corresponding to the hybrid process.

**Table 3.** Different treatment alternatives considered in this work.

Alternative	Treatment	Vacuum production (Permeate)	Membrane Material
A11	Dist./Inc. Cement kiln	-	-
A12	Dist./Inc. WSI	-	-
A21	Dist./Pervaporation	Vacuum Pump/Refrig. System	Ceramic
A22	Dist./Pervaporation	Steam-jet ejector system	Ceramic
A23	Dist./Pervaporation	Vacuum Pump/Refrig. System	Polymeric
A24	Dist./Pervaporation	Steam-jet ejector system	Polymeric

the mixture acetone-water that shows an inflection point in its equilibrium curve at an acetone mole fraction of 0.4019.

Simulations in terms of the rectification advance at different operating policies (i.e., constant reflux ratio or constant distillate composition) are performed with the aid of the software CBD Toolkit 4.0.<sup>[39]</sup>

Once results at the conceptual model level are obtained, the vapor flow rate  $V$  (kmol/h) must be iteratively calculated for given values of the batch size  $M_0$  (kmol) and the operating time  $t_D$  as explained in Section 7.3 of Torres and Espinosa.<sup>[11]</sup> For the integration of equation (13) in the mentioned paper,<sup>[11]</sup> the instantaneous reflux ratio is calculated by multiplying the instantaneous minimum reflux ratio by 1.2.

The number of trays is estimated with the aid of DISTIL<sup>[40]</sup> from  $(x_B^0, R(0))$  in order to achieve the selected distillate composition  $x_D$  for the first cut at column top. Since the instantaneous separation at the very beginning of the operation requires the greatest number of theoretical stages, this criterion is adopted to estimate the optimal value for this design variable. Finally, the simulation of the instantaneous separation in Aspen Hysys<sup>[29]</sup> for the initial conditions is used to determine both the column diameter and the type of internals using the tool Tray Sizing.<sup>[29]</sup>

### Validation of the conceptual model through rigorous simulation

Once the design variables are estimated at the conceptual model level, rigorous simulations of the distillation task with Aspen Batch Distillation<sup>[29]</sup> were performed in order to validate the results at the conceptual model level and to include the hold-up issue.<sup>[30]</sup>

### Conceptual model for the pervaporation task

In the typical arrangement of a staged pervaporation process, a heat exchanger is placed either after a constant

temperature drop of the liquid mixture or a constant membrane area. The decrease in the temperature, which results in a decrease of the driving force for the permeation process, is due to the change of state of the permeating components, which take their vaporization heat from the retentate liquid. An additional drop in the driving force for the separation is caused by a concentration decrease along the module of the preferentially permeating component in the liquid mixture.<sup>[41]</sup>

Bausa and Marquardt<sup>[42]</sup> introduced the concept of minimum membrane area, a limiting design requiring an infinite number of heat exchangers for the membrane unit in order to simplify the design process. In this case, the membrane model is integrated by considering the maximum driving force (i.e., no liquid temperature drop) at each volume element of the membrane unit the composition of the product in the retentate achieves the specified value. The minimum membrane area was multiplied by a fixed factor of 1.25 to obtain a reasonable value for the actual membrane area; this factor is in the recommended interval by the mentioned authors.<sup>[42]</sup>

As shown in Figure 1(b), the membrane system is formed by a feed tank, the membrane unit itself, and a recirculation pump. Genduso et al.<sup>[43]</sup> proposed to model this system from an equation which is similar to the Rayleigh equation for batch distillation; however, the thermodynamic equilibrium relationship between the vapor and liquid phases is replaced by the separation performance of the membrane. The main model assumption is that the time required for liquid circulation is negligible compared with the processing time. Thus, the instantaneous membrane performance is calculated at the feed tank conditions. Applied to the exploration of a multi-stage-batch-pervaporation (MSBP) unit, it was concluded<sup>[43]</sup> that the approach could be used in the screening of membrane materials replacing the typical PSI.

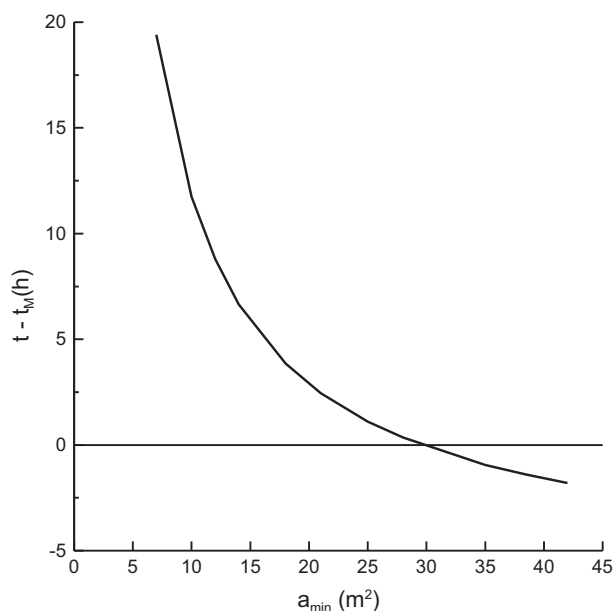
In this work, the mentioned assumption is removed, allowing the variation of the retentate composition along the membrane unit while maintaining the driving force for the temperature at its maximum value (i.e., no liquid temperature drop along the membrane module). While the mass balance in the feed tank is modeled through a set of differential equations, the pervaporation unit of a given membrane area is modeled by integrating a spatially one-dimensional isothermal model of the unit involving a semi-empirical local flux model accounting for the mass transfer through the membrane. The volumetric flow rate of the recirculation pump is fixed according to Reynolds numbers achievable in the module geometry chosen.



### Algorithm based in the improved memory method to estimate the minimum membrane area calculation

Figure 3 shows the time needed for a given separation as a function of the required minimum membrane area. The membrane selected is the HybSi membrane from Pervatech (the Netherlands). Simulations of the system feed tank-pervaporation unit for different membrane areas were performed for an arbitrary feed amount of 100 kmol with an acetone mole fraction of 0.85, which in turn is the desired composition of the first cut of the distillation task. In all cases, integration in time was stopped when the mole fraction of acetone in the feed tank achieved a value equal or greater than 0.97 (99 wt. %). For the base case, the minimum area  $a_{min}^*$  corresponding to the selected operating time  $t_M$  of 6 h is 29.7 m<sup>2</sup>.

In Figure 3, evaluation of the minimum membrane area  $a_{min}^*$  for the operation time  $t_M$  is the root of the error function  $t - t_M = f(a_{min})$ . Thus, methods for finding the root of a non-linear function can be used to calculate the value of the design variable for the base case. We recommend the use of the improved memory method.<sup>[44]</sup> The method is used to solve nonlinear equations of the form  $f(x) = 0$  by approximating the inverse function of  $f(x)$ , namely  $x = \Psi(f)$ , through inverse interpolation with continued fractions and evaluating the inverse function for  $f = 0$ . The  $x$  found value is the root of the nonlinear equation, that is,  $x^* = \Psi(0)$ . The algorithm requires the evaluation of a series of points  $(x_0, f_0)$ ,  $(x_1, f_1)$ , ...,  $(x_n, f_n)$ , and it demands the “smallest number of function evaluations



**Figure 3.**  $t - t_M$  (h) versus  $a_{min}$  (m<sup>2</sup>) for the base case. The desired time  $t_M$  is set to 6 hours. HybSi ceramic membrane, tubular module. At  $t = t_M$ ,  $a_{min}^*$  is 29.7 m<sup>2</sup>.

in comparison with other methods” as a consequence of using the information from previous iterations to generate greater order estimations of the inverse function (lineal, quadratic, etc.). Therefore, the number of dynamic simulations of the membrane task needed to calculate  $a_{min}^*$  are maintained at its minimum value.

Once the minimum area requirement for the base case  $a_{min}^*$  is obtained, the minimum area for the actual design  $A_{min}^*$  can be calculated from the ratio between the product amount of the actual design (calculated from the overall mass balance corresponding to the hybrid process, Figure 1 (b)) and that of the base case (obtained from the dynamic simulation for  $a_{min}^*$ ), that is,  $A_{min}^* = a_{min}^* \text{Product}/\text{product}$ . From known values of the feed to the process ( $F = 72.9$  kmol,  $x_A^F = 0.3$ ), the composition of the still at the end of the distillation task ( $x_A^{\text{Residue}2} = 0.003$ ) and the mole fraction of acetone in the product tank at the end of the membrane task ( $x_A^{\text{Product}} = 0.97$ ) it is possible to calculate the corresponding molar amounts of the residue ( $\text{Residue}_2 = 50.6$  kmol) and product ( $\text{Product} = 22.3$  kmol).

It is noteworthy that the ratio between the product amount for the actual design and that of the case base determines not only the area requirement ( $A_{min}^* = 7.6$  m<sup>2</sup>) of the actual design but also the molar amounts of the feed and permeate for the actual design.

The vacuum production necessary to maintain a low pressure in the permeate side is considered with two alternatives for vacuum production, namely i) vacuum pump/refrigeration system and ii) steam-jet ejector system.

### Conceptual model for the vacuum production task: vacuum pump/refrigeration

The vacuum pump/refrigeration system is formed by a condenser followed by a vacuum pump. The aim of this system is to recover the major part of permeate as a liquid while decreasing the charge of the gas evacuated by the vacuum pump. The permeate stream entering to the condenser is first cooled from the operating membrane temperature to the dew point and then condensed until reaching the bubble point of the mixture, which is a function of the instantaneous composition of the permeate stream. A cooling service fluid is required to achieve the condensation given the relatively low value of the permeate pressure (7.5 kPa). In this case, the condenser is coupled with a vapor compression refrigeration cycle using propane as refrigerant.

Note that an inward leakage of air into the equipment under vacuum is unavoidable. Given that the air remains always in the vapor phase, its mole fraction increases along the condenser. Particularly, at the condenser end, the vapor-liquid equilibrium is more

affected by the presence of air so that the bubble point of the mixture is lower than that of the binary mixture. A technical relevant aspect is the freezing point of the binary mixture, which depends on its composition and acts as a lower bound for the minimum condensation temperature achievable in the condenser at the given permeate pressure.<sup>[45]</sup>

To perform an appropriate description of the phase change of the mixture, a multi-node model for the condenser is adopted.<sup>[46]</sup> Given that inward leakage of air depends on the volume under vacuum an iterative procedure is required to solve the material and energy balance together with the design equations for condenser area and volume (including the membrane module).<sup>[45]</sup>

The best operational conditions for this system are obtained by solving an optimization problem with an objective function that minimizes the overall annual cost of the system. The optimization variables are the condensation temperature at the end of the condenser, and the refrigerant pressures in the vapor compression refrigeration system.

### Conceptual model for the vacuum production task: steam ejector

If the permeate stream has a low solvent content, this stream also has a low commercial value. In this case, it is not necessary to recover the solvent in the distillation task. However, the vacuum level should be maintained. For this purpose, a conventional steam-jet ejector system is adopted as an alternative with a lower investment cost than that of the vacuum pump/refrigeration system. Note, however, that the steam diluted permeate stream requires a biological treatment prior to be discharged. To this end, it will be mixed with the still content at the end of the distillation task in the next batch.

In order to model this system with the aid of short-cut models, the feed must be converted into an air equivalent in standard conditions.<sup>[47]</sup> The data presented by Coker<sup>[47]</sup> for steam and water cooling consumption were correlated for a system formed by three ejectors with two inter-condensers.

### Economic analysis

The economic analysis was made by calculating the annualized investment cost and the annual operating cost, based on the methodology proposed by Seider et al.<sup>[48]</sup> Quasi-optimal values for design and operation variables obtained at the conceptual design level<sup>[24]</sup> are used as input data to perform the economic assessment of each alternative. The total capital investment is annualized taking ten years as lifetime and with 10%

interest rate. The annual utilities consumption are calculated considering the respective unit operating cycle time in a time-horizon of 360 days/year. A more detailed description can be found in the Supplementary material.

### Environmental assessment

The goal of life cycle assessment is to evaluate the environmental impact of the alternatives studied for one year of operation. Life cycle inventory (LCI) was created using the quasi-optimal values for the utilities, that is, cooling water, electricity, and steam needed for distillation and pervaporation.<sup>[24,49]</sup> In the LCI, solvent production and waste water treatment are also included. Inventories corresponding to the incineration of the first cut of the distillation step in Alternatives A11 and A12 and treatment of column residues in all alternatives are calculated with the aid of Ecosolvent v.1.0.1, an LCA free-software developed by Capello et al.<sup>[50,51]</sup>

Finally, the environmental impact of each alternative is obtained with the aid of the software SimaPro 7.3.<sup>[38]</sup> Marginal suppliers are used in consequential LCA. The hierarchist (H) perspective was chosen in the analysis.

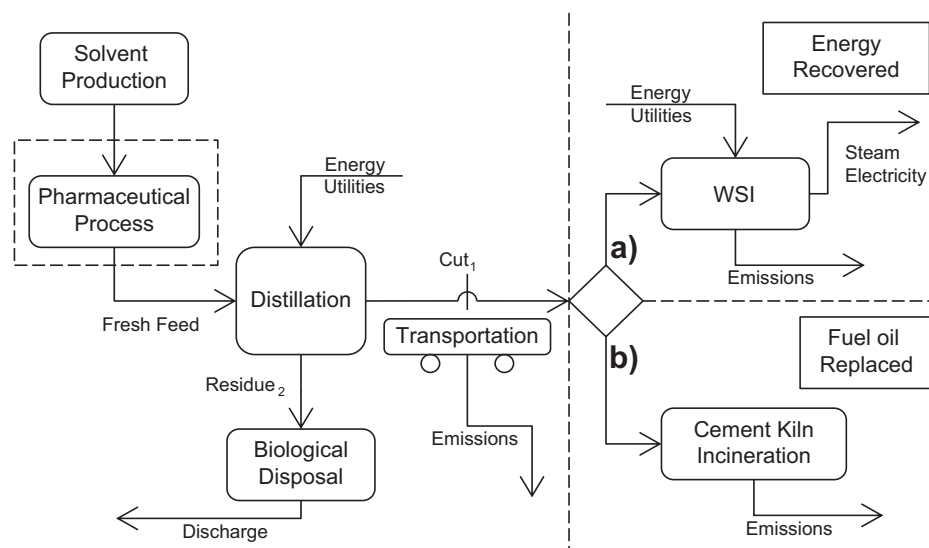
### Incineration alternatives

The inventory related to the alternative involving incineration is estimated following the same approach of the work of Meyer et al.<sup>[24]</sup> Two different models are studied: a cement kiln<sup>[25]</sup> and a waste solvent incinerator.<sup>[27]</sup> A stream with the same concentration of that of Cut<sub>1</sub> but with an overall amount calculated on a yearly basis is considered to be sent to the incinerators. Figure 4(a)–(b) shows the system boundaries of the analysis.

The solvent incineration model used in this work considers a large solvent incineration plant, where liquid wastes, including spent organic solvents, distillation residues, mother liquors, waste oils, and highly organic charged wastewaters are disposed<sup>[50]</sup> and steam and electricity are co-products obtained in this incineration plant. The total environmental impact ( $I_{inc}$ ) is the summation of the impacts (positive values) caused by the use of supplemental fuel oil ( $I_{oil}$ ), ancillaries ( $I_{anc}$ ), the emission of CO<sub>2</sub> ( $I_{CO_2}$ ), other emissions ( $I_{em}$ ), and the reduction of environmental burdens (negative values) from the energy by-products ( $I_{energy}$ ):

$$I_{inc} = I_{oil} + I_{anc} + I_{CO_2} + I_{em} + I_{energy} \quad (1)$$

In a cement kiln plant, the waste solvents are used as fuel in cement production. Thus, fossil fuels such as coal and heavy fuel oil are saved. Furthermore, in this



**Figure 4.** Flow charts for Alternative 1 considering two incineration alternatives: (a) a WSI plant and (b) a cement kiln.

model, changes in the emissions as a consequence of substituting fossil fuels with waste solvents are calculated. Therefore, all emissions are expressed as differences. This model was adjusted with regard to the calculation of  $\text{NO}_x$  emissions.

The amount of fossil fuel substituted and changes in emissions of  $\text{CO}_2$ ,  $\text{NO}_x$ , and metals, such as copper or cadmium serve as inventory parameters quantified for this model.<sup>[49]</sup> Thus, the total environmental impact of the waste-solvent incineration in cement kilns ( $I_{\text{cement}}$ ) is composed of the environmental impacts of the changes in  $\text{CO}_2$  emissions ( $I_{\text{CO}_2}$ ),  $\text{NO}_x$  emissions ( $I_{\text{NO}_x}$ ), metal emissions ( $I_{\text{metals}}$ ), and the environmental benefits (negative value) from fossil fuel substitution ( $I_{\text{fuel}}$ ) according to equation (2):

$$I_{\text{cement}} = I\Delta_{\text{CO}_2} + I\Delta_{\text{NO}_x} + I\Delta_{\text{metals}} + I_{\text{fuel}} \quad (2)$$

Because the formation of  $\text{NO}_x$  in cement kilns is complex and incompletely understood,<sup>[52]</sup> the conversion rate of fuel nitrogen to  $\text{NO}_x$  is modeled as an uncertain parameter. Ranges for coal (20% to 48%), heavy fuel oil (56% to 72%), and waste solvent (52% to 92%, which corresponds to the conversion rates for N in light fuel oil and other liquid fuels) are used.<sup>[50]</sup> Thermal  $\text{NO}_x$ , which is produced when nitrogen and oxygen in the combustion air supply combine at high flame temperature, contributes the most to the total  $\text{NO}_x$  emissions from clinker kilns.<sup>[52]</sup> Thermal  $\text{NO}_x$  emissions, however, do not need to be considered in the model, as the net calorific value is not influenced by fuel substitution. The efficiency of the  $\text{NO}_x$  reduction facility is modeled as a variable with value between 0% (in case this equipment is missing) and 80%.

### Solvent recovery alternatives

Impacts related to the following tasks are considered for the solvent recovery alternative: i) solvent production, ii) pre-concentration step, iii) pervaporation task, iv) vacuum production, and v) biological disposal. Figure 5 (a)-(b) show the inputs considered:

All these steps bring a burden to the environment, while the benefits are gained by the possibility to reuse acetone after the pervaporation unit. This is one of the most important differences with the other alternative. Indeed for WSI, the benefits are in the production of steam and electricity; in a cement kiln, the benefits are in the substituted fuels and the avoided emissions. Credits to the environment are given for the possibility to reuse the solvent, corresponding to its avoided production.

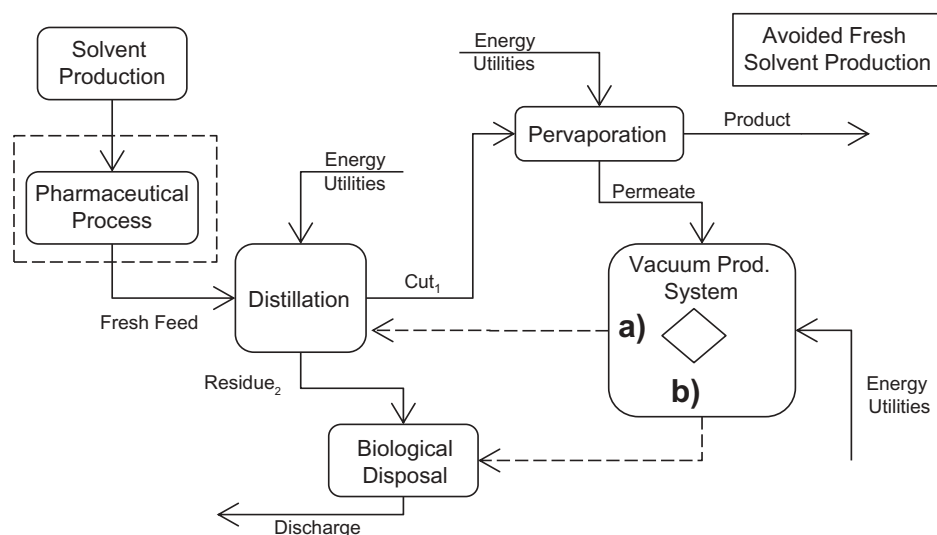
### Biological disposal model

In the LCA analysis, the impact caused by the treatment of residue of the distillation task is also considered. To estimate the impact of this treatment technology, Ecosolvent<sup>[49]</sup> is used. Nevertheless, this facility does not produce a large impact, and the amounts to be treated are almost the same in all alternatives. Thus, it does not play a decisive role in the selection of the alternatives.

### Impact methods and software

ReCiPe<sup>[53]</sup> method is used for estimating the environmental burdens of the alternatives considered in terms of the human health, ecosystem, and natural resources. In Ecosolvent software,<sup>[50]</sup> ReCiPe is not available, thus in the first assessment Eco-Indicator 99 is used as environmental method. ReCiPe 2008,<sup>[53]</sup> unlike other





**Figure 5.** Flow charts for Alternative 2 considering two alternatives of vacuum production: (a) a vacuum pump/refrigeration system and (b) a steam-jet ejector system.

approaches (Eco-Indicator 99, EPS Method, LIME, and Impact 2002+), does not include potential impacts from future extractions in the impact assessment but assumes such impacts have been included in the inventory analysis. The environmental impact assessment was undertaken using the ReCiPe 2008 v.1.04 method from SimaPro 7.3<sup>[38]</sup> software package. ReCiPe 2008 includes three endpoint categories and eighteen midpoint categories. Midpoints are accounted with their own characterization factors. The endpoints are presented as single score.<sup>[53,54]</sup>

## Results and discussion

In this section, the results of each operational unit are reported. Afterwards, the economic and environmental analyses are performed to draw the conclusions for the assessment of the alternatives to treat this mixture.

### Pervaporation

Table 4 shows the mass balances corresponding to the base case and the actual design for the HybSi ceramic membrane. As mentioned in Section 2.3.1, the ratio between the product amount for the actual design and that of the case base (i.e., 0.26) determines not only the molar amounts of the feed and permeate of the actual design but also the area requirement (7.6 m<sup>2</sup>). A module of 12 tubular units (total area 8.4 m<sup>2</sup>) arranged in series is then adopted as the minimum area requirement for the separation. The operating time  $t_M$  changes from 6 to 5.6 hours. The cumulative condensation power is about 6.35 kW but a maximum value of

**Table 4.** Mass and energy balance for the membrane task (HybSi ceramic membrane, tubular module). Area and molar amounts for the feed and permeate of the actual design are calculated from the ratio **22.3/87.3**.

		Feed	Product	Permeate
Base Case	Amount (kmol)	100	87.3	12.7
	$x_A$ (mol/mol)	0.85	0.97	0.03
	$a_{min}^*$ (m <sup>2</sup> )		29.7	
	Condens. Power (kW)	Average 23.4 Max. 61.7		
	Operating time $t_M$ (h)	6		
Actual Design	Amount (kmol)	25.6	<b>22.3</b>	3.3
	$x_A$ (mol/mol)	0.85	0.97	0.03
	$A_{min}^*$ (m <sup>2</sup> )/Corrected	7.6/8.4		
	Condens. Power (kW)	Average 6.35 Max. 16.6		
	$t_M$ (h)/Corrected	6/5.6		

16.6 kW is achieved at the beginning of the operation. A volumetric flow rate of 2 m<sup>3</sup>/h was adopted for the recirculation pump to guarantee turbulent flow inside the tubes ( $Re \geq 19000$ ). In this way, both concentration polarization and limit fouling are prevented.

The overall balance of the membrane task and its corresponding area requirement can be calculated in advance even when the distillation task design is not still accomplished. The permeate amount is sufficiently low to predict a pseudo-steady state for the distillation task almost identical to that of the alternative distillation/incineration as it will show in Section 3.2.

Table 5 shows the results obtained for the polymeric membrane. The volumetric flow rate of the recirculation pump is now fixed to a value that assures a Reynolds number of about 3600 inside the modules. The polymeric membrane requires 25 times higher minimum area than the ceramic membrane. This large difference for the respective operating conditions is mainly due to the difference in selectivity and flux to

**Table 5.** Mass and energy balance for the membrane task (polymeric membrane, plate and frame module). Area and molar amounts for the feed and permeate of the actual design are calculated from the ratio **22.3/10.3**.

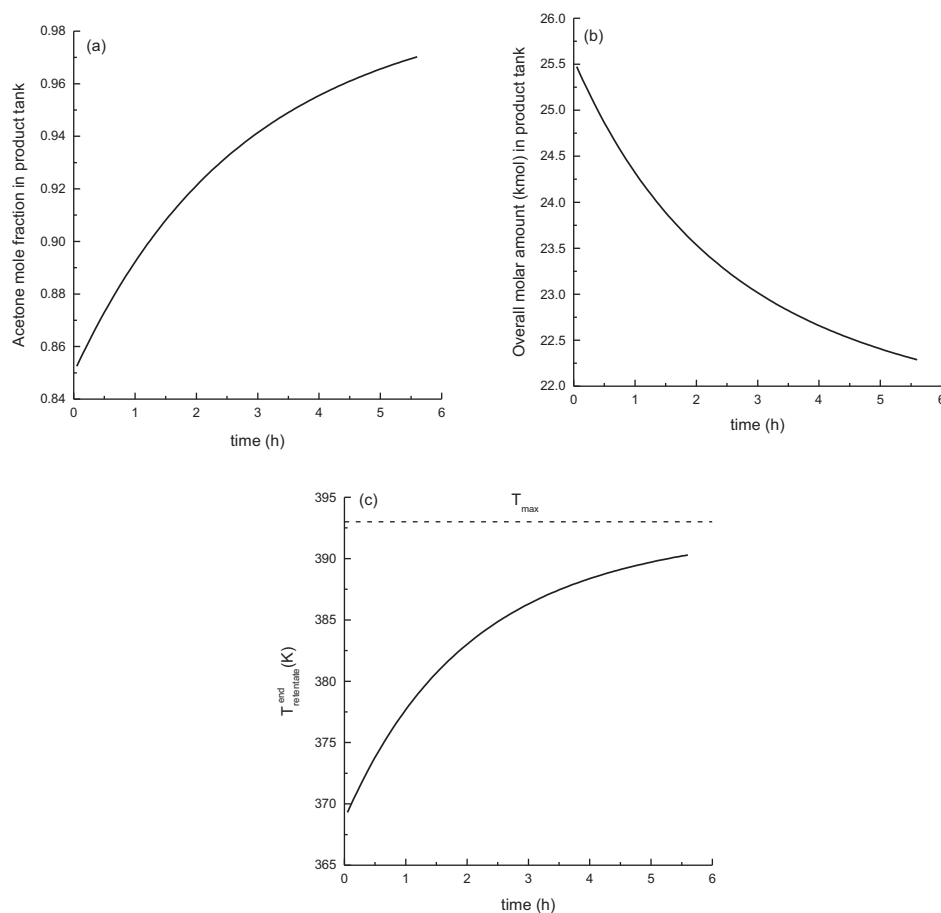
		Feed	Product	Permeate
Base Case	Amount (kmol)	25	10.3	14.7
	$x_A$ (mol/mol)	0.85	0.97	0.76
	$a_{min}^*$ (m <sup>2</sup> )		93	
	Condens. rate (kW)	Average 22.9 Max. 60.0		
	Operating time $t_M$ (h)	6		
Actual Design	Amount (kmol)	54.1	<b>22.3</b>	31.74
	$x_A$ (mol/mol)	0.85	0.97	0.76
	$A_{min}^*$ (m <sup>2</sup> )/Corrected	201.3/204		
	Condens. rate (kW)	Average 50.0 Max. 129.3		
	$t_M$ (h)/Corrected	6/5.7		

achieve the desired separation requirements (Table 1). Consequently, for the polymeric membrane the high values for the membrane area and the permeate amount require an expensive process that discourages its use for acetone recovery at least at the actual operating conditions.

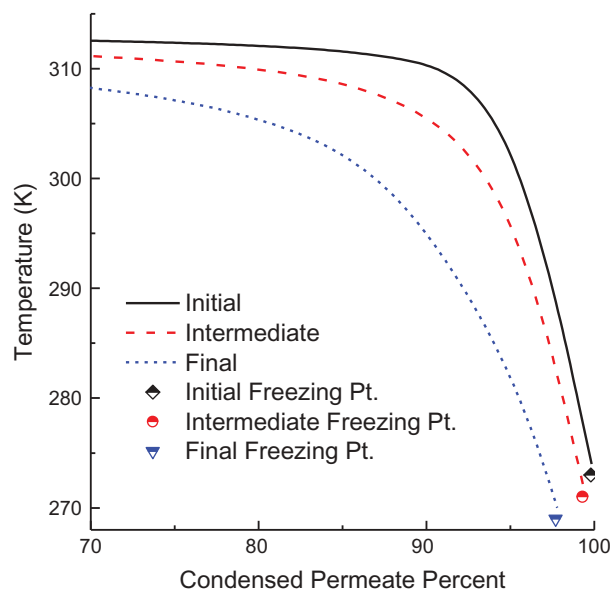
Figure 6(a)-(c) shows the time evolution of the acetone mole fraction in the product tank, the overall molar amount in the product tank and the minimum

temperature that could be achieved for the retentate stream leaving the HybSi membrane module. The lowest temperature value is achieved at the operation beginning and it is necessary to estimate the heat exchange area of the retentate re-heater. At this time, the heating rate achieves a maximum value of 16.6 kW (see Table 4).

Regarding the vacuum production task, Figure 7 shows the heat release curves in the condenser (Vacuum Pump/Refrigeration System) corresponding to three different operation times. Figure 7 reflects the time-dependent behavior of these curves. The bottleneck operation occurs at the operation beginning. Therefore, the condenser area and another equipment sizes are calculated from the conditions corresponding to the bottleneck. Especially at the end of the operation it is not possible to achieve a complete condensation of the permeate. The barrier that avoids complete condensation is established by the temperature in the freezing point, as explained in Section 2.3.2. About 98% of the total of permeate is condensed but this only represents 80% of the acetone initially contained.

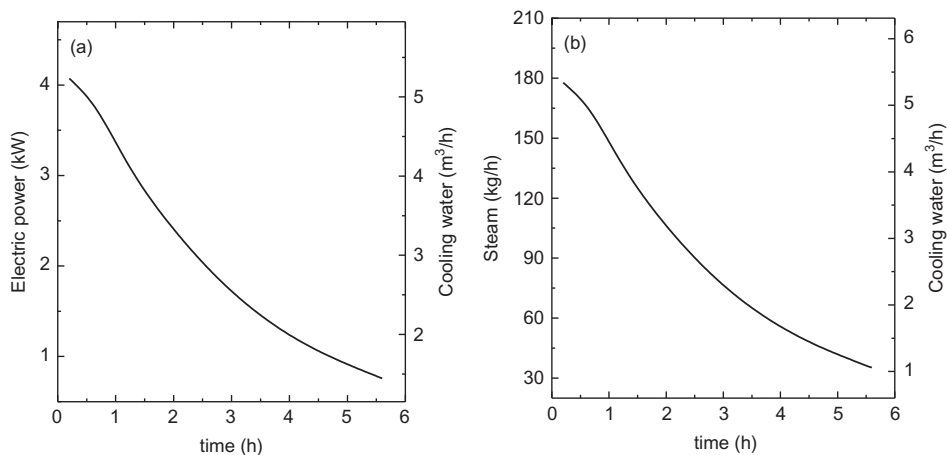


**Figure 6.** Evolution of (a) the mole fraction of acetone in the product tank. (b) the overall molar amount in the product tank. (c) the minimum temperature achievable in the retentate stream leaving the module. Maximum operation temperature is set to 393.14 K. HybSi membrane (Pervatech).



**Figure 7.** Heat release curves in the condenser at initial (0 h), intermediate (3 h) and final (6 h) operation time with their respective freezing points (for a better appreciation, the interval from 70 to 100% is only displayed). HybSi membrane (Pervatech).

Figure 8(a) shows the utilities consumption corresponding to the vacuum pump/refrigeration system. Both the electric energy and the water consumption have a decreasing behavior in time, following the same trend that the permeate stream flow rate. Figure 8(b) shows the time-dependent steam and water consumption profiles for the steam-jet ejector system. Similar to the vacuum pump/refrigeration system, the utilities consumption decreases in time. This reflects that the flow rate of the permeate, which in turn varies from 1.5 to 0.2 kmol/h, is the most determinant variable to calculate the operating costs of the vacuum production task.

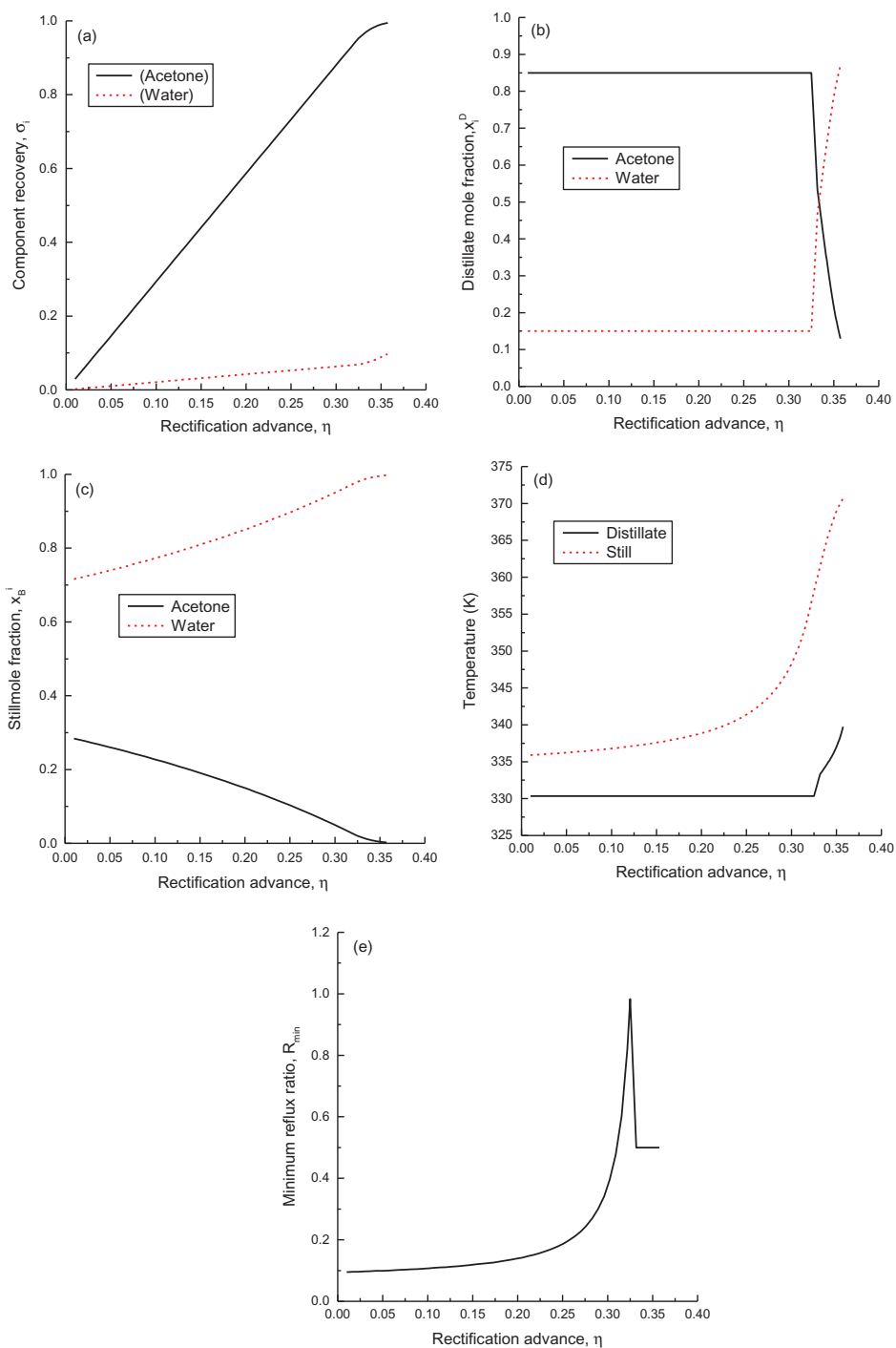


**Figure 8.** Instantaneous utilities consumption for: (a) the vacuum pump/refrigeration system. (b) the steam-jet ejector system. HybSi membrane (Pervatech).

## Distillation

Results obtained from the integration of the conceptual model, that is, recoveries of acetone and water in the distillate, distillate and still compositions, distillate and still temperatures, and instantaneous minimum reflux ratio in function of the rectification advance  $\eta$  are shown in Figure 9(a)–(e), respectively. During the first cut, the distillate composition was set at 85 mol % of acetone (Figure 9(b)). The selected distillate composition enabled the achievement of three objectives: i) obtaining a distillate of high calorific value for the incineration alternatives, ii) a decrease of the separation effort in the subsequent pervaporation task, iii) a decrease in the separation effort in the distillation task itself. For each instantaneous still composition, the algorithm estimated the instantaneous minimum reflux ratio necessary to achieve the desired acetone mole fraction in the distillate. The rectification advance  $\eta$  was varied until achieving an acetone “per-pass” recovery of 95% measured as the recovery of the acetone contained in the column charge, which in turn is composed by the fresh feed, the second cut and the condensed permeate from the membrane unit (Figure 1). As shown in Figure 9(e), the reflux ratio was continuously growing up during the first cut. In order to achieve a water concentration of 99.7 mol % in the boiler at the end of the operation (see the reached value in Figure 9(c)), a second cut operated with a constant reflux policy (0.5) was implemented. The second cut was recycled to the next batch as shown in Figure 1(a), in order to avoid acetone losses. The selected “per-pass” recovery of the solvent of 95% minimized the amount of the second cut and hence, the amount of feed in the still in pseudo-steady state.

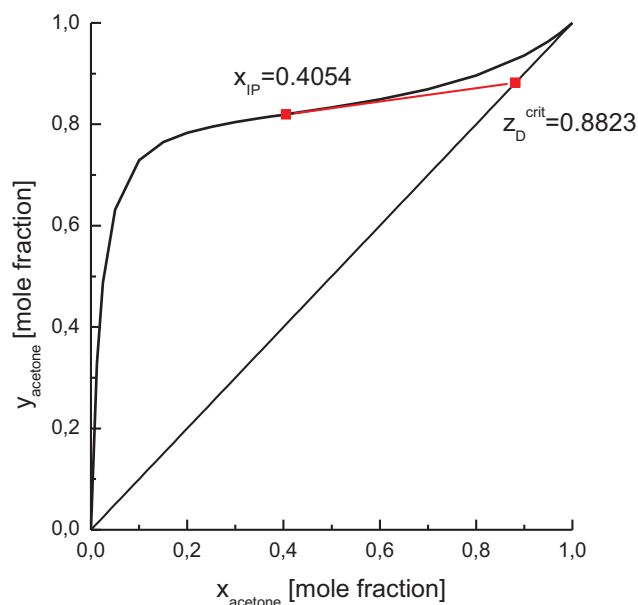
The choice of 85 mol % as distillate composition for the first cut can be clarified by analyzing Figure 10, which



**Figure 9.** Results obtained from the conceptual model of the distillation task. Profiles (a) to (e) correspond to Alternative A21: Distillation followed by pervaporation with the ceramic membrane. A vacuum pump/refrigeration system is used as condensation technology for vacuum production.

shows the vapor-liquid equilibrium diagram for the acetone-water system. It is noteworthy that the  $y$  vs.  $x$  curve of the mixture has an inflection point  $x_{IP}$ , 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  $z_D^{crit}$  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. Moreover, given the shape of the vapor-liquid equilibrium curve, the energy demand of the distillation task in such a region will be low. Producing acetone in high purity would require, on the other hand, not only high



**Figure 10.** Diagram  $y$  vs.  $x$  for acetone-water mixture at 101.3 kPa.  $x_{IP}$  represents the composition of the mixture at the inflection point of the equilibrium curve.

instantaneous reflux ratios but also demand a significantly high number of theoretical trays due to the appearance of a tangent pinch point.<sup>[12]</sup> In such a case, distillate purity control is also an issue due to the occurrence of a zone of constant composition near the rectifier top. For these reasons, the alternative of using only distillation to recover acetone is not considered along the paper.

Tables 6 and 7 show the overall mole balance in the pseudo-steady state together with the main operating and design variables for all the alternatives considered. A pseudo-steady state operation is achieved in each case after several batches are run. Main differences among the different alternatives are given in both the amount and composition of the mixture to be treated, which can be different due to the presence of a recycle stream. For the sake of simplicity, only the case of the Alternative A21 is reported in Figure 9. Furthermore, no significant differences were found for the other cases.

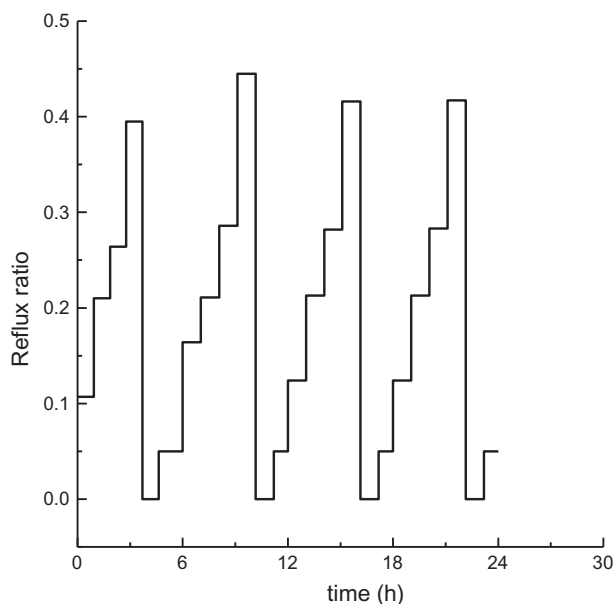
**Table 6.** Overall mole balance for the distillation task in a pseudo-steady state corresponding to an acetone “per-pass” recovery of 95% at the end of the first cut.

Alternative		Column charge	Cut <sub>1</sub>	Residue <sub>1</sub>	Cut <sub>2</sub> (Recycle)	Residue <sub>2</sub>
A11, A12, A22, and A24	Overall amount (kmol)	75.3	25.6	49.7	2.4	47.3
	Acetone (mol/mol)	0.31	0.85	0.02	0.41	0.003
	Water (mol/mol)	0.69	0.15	0.98	0.59	0.997
A21 (Ceramic membrane)	Overall amount (kmol)	78.7	25.6	53.1	2.5	50.6
	Acetone (mol/mol)	0.29	0.85	0.02	0.37	0.002
	Water (mol/mol)	0.71	0.15	0.98	0.63	0.998
A23 (Polymeric membrane)	Overall amount (kmol)	106.6	52.2	54.4	3.9	50.5
	Acetone (mol/mol)	0.44	0.85	0.04	0.55	0.003
	Water (mol/mol)	0.56	0.15	0.96	0.45	0.997

The tool Tray Sizing<sup>[29]</sup> recommended the adoption of a packed column with a diameter of 0.3048 m considering the relatively low vapor flow rates involved in all studies.

Aspen Batch allowed to run the operation several times in series. Figure 11 shows the time evolution of the reflux ratio for a feasible “per-pass” recovery of acetone in the first cut of 90%. It was found that a pseudo-steady state was achieved after the fourth batch.

Table 7 also shows the comparison between the conceptual model (CM) and the simulation in Aspen Batch Distillation<sup>[29]</sup> in terms of the design and operation variables of the batch rectifier for the different alternatives studied. The results obtained by rigorous simulation are almost coincident with those obtained from the conceptual model. While the maximum relative error in the steam consumption was about 15%, a relative error as low as 8% was achieved in the cooling water requirement.



**Figure 11.** Time evolution of the reflux ratio obtained from rigorous simulations in Aspen Batch Distillation.



**Table 7.** Design and operation variables of the batch rectifier for the different alternatives studied. Results obtained from both the conceptual model (CM) and Aspen Batch Distillation are reported.

	Alternative				
	A11, A12, A22 and A24 "Standalone"		A21 "Ceramic"	A23 "Polymeric"	
	CM	Aspen	CM	Aspen	CM
Vapor flow rate (kmol/h)	5.7	5.7	5.9	5.7	11
Condenser area (m <sup>2</sup> )	4.0	4.4	4.2	4.15	7.7
Evaporator area (m <sup>2</sup> )	2.3	2.5	2.4	2.5	4.3
Horizontal vessel volume (m <sup>3</sup> )	3.3	3.6	3.5	3.57	5.9
Packed height (m)	3.5	3.5	3.5		3.5
Packed diameter (m)	0.305	0.305	0.305	0.305	0.305
Cooling water (m <sup>3</sup> /year)	6000	6500	6200	6500	11500
Steam (kg/year)	225000	268000	235000	272000	436000

The results predicted by the model for the distillation task corresponding to the alternative distillation coupled with the polymeric membrane show the highest energy consumption. This low performance is triggered by the low performance of the polymeric membrane given by the large amount of permeate to be recycled (see Table 5). On the other hand, no meaningful differences are found for the other two distillation alternatives since the recycled amount from the ceramic membrane (permeate amount) is rather low. According to these results, the rest of the analysis focuses on the alternatives distillation/incineration and distillation/pervaporation with the ceramic membrane.

### Economic figures

Quasi-optimal values for design and operation variables obtained at the conceptual design level were used as input data to perform the economic assessment of each alternative. Investment and operation costs were calculated on a yearly basis. Table 8 makes a comparison between Alternatives A11 and A12; namely, distillation followed by incineration in a cement kiln and in a waste solvent incinerator (WSI), respectively. Table 8 indicates that the incineration cost in a waste solvent incinerator covers approximately half of the overall cost of Alternative A12. Alternative A11 (457 U\$\$/ton) is

**Table 8.** Annualized investment and operating costs (10<sup>3</sup> U\$\$/year) for the alternatives distillation/incineration.

	Alternative Distillation/Incineration	
	A11	A12
Column investment cost	52	52
Utilities	6.1	6.1
Column residue disposal	4.4	4.4
Transport cost	10.7	10.7
Incineration	71.8	120
General costs	62	62
Overall costs	208	256
Acetone to incineration (t/year)	454	454
Overall costs (U\$\$/t Acetone)	457	563

preferable to Alternative A12 (563 U\$\$/ton) in economic terms given that the cement plant uses the distillate as fuel.

From Table 9, the distillation/pervaporation alternatives are compared only for the case of the HybSi membrane. Here, the investment cost of the pervaporation unit with a steam-jet ejector system (Alternative A22) is lower than that of the membrane unit coupled to a vacuum pump/refrigeration system (Alternative A21). However, the cost of the utilities consumption has the opposite behavior and then the costs of the pervaporation units are balanced. Overall, the cost of Alternative A22 (597 U\$\$/ton) is about 5% lower than that corresponding to Alternative A21 (625 U\$\$/ton).

Among the alternatives, it is concluded that the total cost for the alternatives with pervaporation are higher than those of incineration of distillate. However, the purchase cost of fresh solvent (about 850 U\$\$/ton) must be added to the incineration alternatives.<sup>[41]</sup> Therefore, from an economic point of view the alternative distillation/pervaporation using a steam-jet ejector system for vacuum production is the best choice.

**Table 9.** Annualized investment and operating costs (10<sup>3</sup> U\$\$/year) for the alternatives distillation/pervaporation (HybSi membrane).

	Alternative Distillation/Pervaporation	
	A21	A22
Pervaporation unit investment cost	96.1	85.1
Column investment cost	52.7	52.2
Column utilities	6.4	6.1
Column residue disposal	5.8	7.1
Pervaporation unit utilities	1.9	5.4
Membrane replacement	3.9	3.9
General costs	116	110
Overall costs	283	270
Acetone recovered (t/year)	453	452
Overall recovery costs (U\$\$/t Acetone)	625	597
Payback period* (year)	4	4

\*Annual earnings consider savings due to the avoided purchase of fresh solvent and the avoided disposal cost of the spent solvent.

## Environmental impact

### Input data for alternatives A11 and A12: distillation followed by incineration

The first cut of the distillation task ( $Cut_1$  in Figure 1(a)) is incinerated off-site either in a cement kiln (Alternative A11) or in a waste solvent incinerator (Alternative A12). The column residue is sent to biological disposal on-site. Note that both mass and energy balances shown in Table 10 are given for a batch of 6 hours, 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 m<sup>3</sup> capacity truck are necessary.

### Input data for alternatives A21 and A22: distillation followed by dehydration in a pervaporation unit

The distillate from the distillation operation ( $Cut_1$  in Figure 1(b)) is dehydrated on-site in a membrane unit (HybSi membrane, Pervatech). Both mass and energy balances in Tables 11 and 12 are given for one batch per day, 360 batches per year.

It must be noted that the LCA input data related to the distillation task do not vary among the alternatives while the input data related to the pervaporation task present a difference between the alternatives due to the vacuum production system. While the steam-ejector system demands a large amount of steam, the vacuum pump/refrigeration system has, in comparison, a higher electricity consumption.

### Environmental impact results

Figure 12(a)–(b) show the comparison at midpoint level of the proposed alternatives. Four among the most representative and effective impact categories were chosen, analyzed, and compared in detail: climate change, terrestrial acidification, freshwater ecotoxicity and fossil depletion. In the case of climate change and terrestrial acidification, the estimated environmental impact had the same trend. In these categories, the

**Table 10.** Input data for LCA. Alternatives A11 and A12 (distillation/incineration).

Mass balance per batch, one batch of 6 hours per day, 360 batches/year			
	Feed	Distillate	Residue
Overall amount (kg/batch)	2187	1329	858
Acetone (mass fraction)	0.58	0.95	0.01
Water (mass fraction)	0.42	0.05	0.99
Energy balance per batch, one batch of 6 hours per day, 360 batches/year			
Steam at 2 bar (kg/batch)	625		
Cooling water (m <sup>3</sup> /batch)	16.7		
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)	2550		

**Table 11.** Input data for LCA. Alternative A21 (distillation/pervaporation).

Mass balance per batch, one batch per day, 360 batches/year			
	Feed	Product	Residue
Overall amount (kg/batch)	2187	1272	914
Acetone (mass fraction)	0.58	0.99	0.01
Water (mass fraction)	0.42	0.01	0.99
Energy balance per batch, one batch per day, 360 batches/year			
Distillation column (6 h/batch)			
Steam at 2 bar (kg/batch)	653		
Cooling water (m <sup>3</sup> /batch)	17.2		
Membrane unit (6 h/batch)			
Steam at 4 bar (kg/batch)	57.0		
Cooling water (m <sup>3</sup> /batch)	2.6		
Compressor electricity consumption (kWh/batch)	12.5		
Vacuum pump electricity consumption (kWh/batch)	2.5		
Circulating pump electricity consumption (kWh/batch)	0.2		

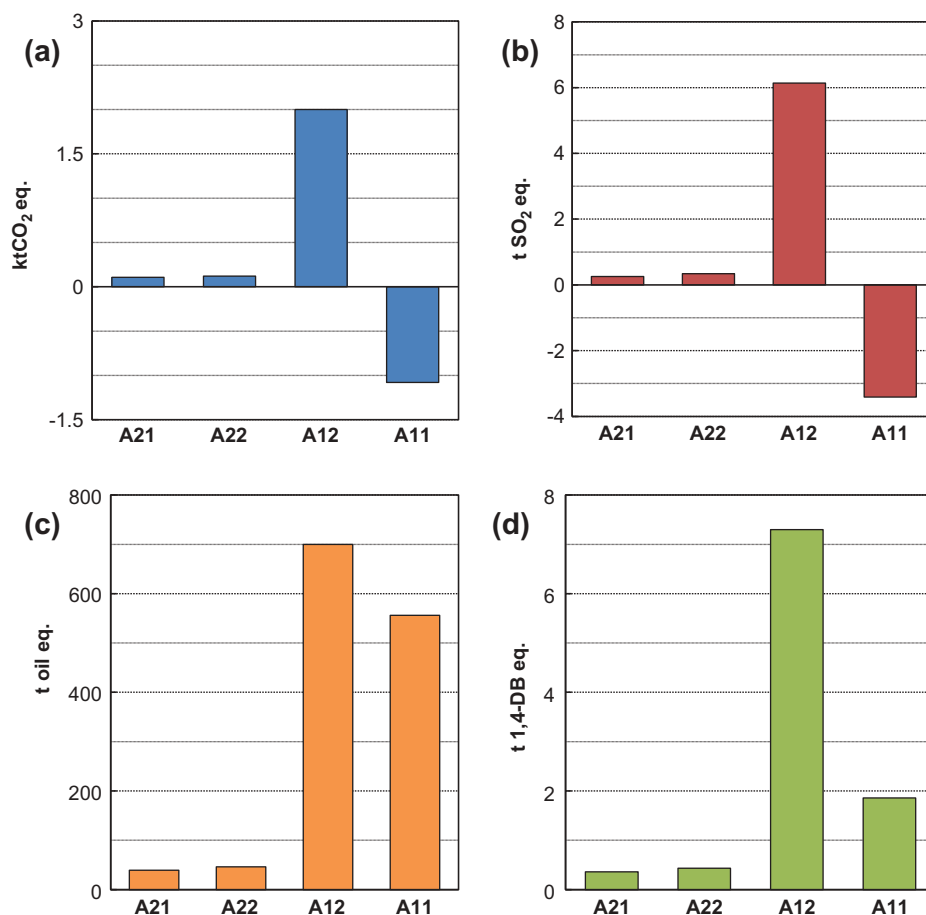
alternative with the WSI, A11, shows a much higher impact than the novel alternatives with pervaporation, A21 and A22. Otherwise, the cement kiln alternative gives benefits to the environment due to the saved fuel in the cement plant.

Taking into account the other two midpoint indicators (fossil depletion and freshwater ecotoxicity, Figure 12(c)–(d), respectively), the recovery solvent alternatives, A21 and A22, have a very lower environmental impact than the incineration alternatives. In particular for the incineration alternatives, the use of a cement kiln implies a lower impact than a WSI.

Results in terms of single score representation (kPoints) are reported in Figure 13(a)–(b). As can be seen, the alternative distillation/WSI (third column) has the highest impact for all considered categories. In particular, it has the highest impact on: particulate matter formation, fossil depletion, and climate change in relation to human health and ecosystem quality. When the alternative distillation/cement kiln is considered (fourth column), it is clear that it still has a very

**Table 12.** Input data for LCA. Alternative A22 (distillation/pervaporation).

Mass balance per batch, one batch per day, 360 batches/year			
	Feed	Product	To biological disposal
Overall amount (kg/batch)	2187	1267	920
Acetone (mass fraction)	0.58	0.99	0.02
Water (mass fraction)	0.42	0.01	0.98
Energy balance per batch, one batch per day, 360 batches/year			
Distillation column (6 h/batch)			
Steam at 2 bar (kg/batch)	625		
Cooling water (m <sup>3</sup> /batch)	16.7		
Membrane unit (6 h/batch)			
Steam at 4/10 bar (kg/batch)	57.0/459		
Cooling water (m <sup>3</sup> /batch)	13.1		
Circulating pump electricity consumption (kWh/batch)	g0.2		



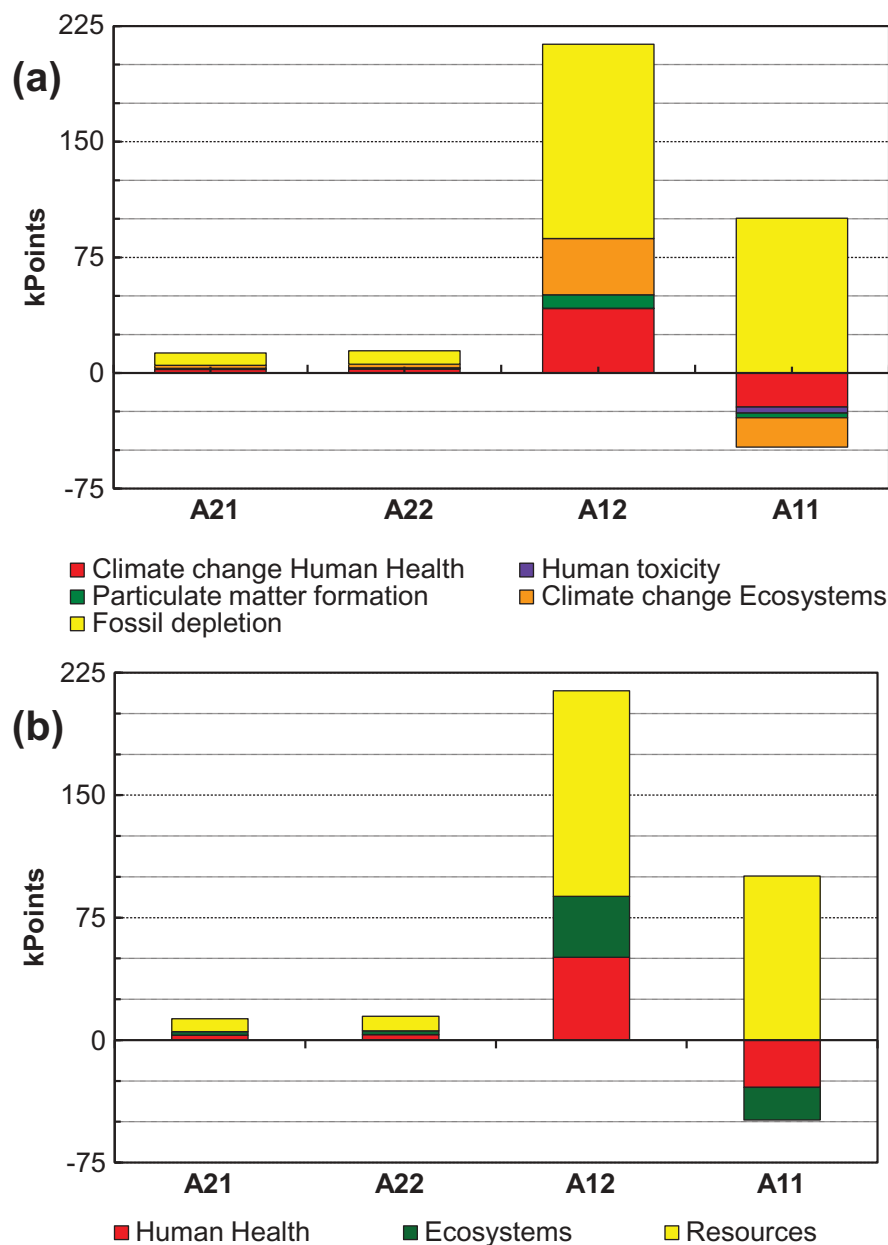
**Figure 12.** LCA results (ReCiPe H/A) for selected categories at midpoint level: (a) climate change, (b) terrestrial acidification, (c) freshwater ecotoxicity and (d) fossil depletion.

high impact on resource depletion. However, due to the avoided coal and heavy fuel, it brings some benefits to the environment in terms of human toxicity, particulate matter formation, climate change-human health and the ecosystem quality. These results are explained by the fact that by using this alternative, the emission of very pollutant components is replaced by those of the concentrated mixture.

For the distillation/pervaporation alternatives corresponding to the HybSi membrane, two key points are highlighted. First, the difference in environmental impact between Alternatives A21 (first column) and A22 (second column) is rather low. Second, the hybrid process coupled to a vacuum pump/refrigeration system shows a slightly lower impact in terms of resources and it can be directly attributed to a lower consumption of utilities, in particular steam, in comparison with that of the recovery process coupled to a steam-jet ejector system as it is shown in Tables 11 and 12. Furthermore, no remarkable differences were found between the distillation tasks in terms of both steam and cooling water demand given the low permeate amount leaving the membrane module in the previous batch.

Finally, when Alternative A21 is compared with Alternative 12, it is also evident that in terms of depleted resources, the hybrid process coupled to a vacuum pump/refrigeration system shows a reduced impact due to the solvent recovery. However, although the impact on human health and ecosystem quality is close to zero, Alternative A21 does not show any benefits, as in the case of the alternative distillation followed by incineration in a cement kiln. Therefore, deciding on alternative of incineration or solvent recovery as being the best option mainly depends on the category on which the focus is placed.

It has to be underlined that these results might show some differences for the incineration alternatives when instead of the model of Capello et al.<sup>[50]</sup> other and more accurate models would be used. In particular, for two main reasons: i) the use of additional fuel, for Alternative 11, to burn the mixture it has to be verified, even because the concentration of acetone sent to the incinerator is very high and ii) the emissions of the NO<sub>x</sub> in cement kiln as also explained by Vermeulen et al.<sup>[55]</sup> have to be considered taking into account properly the process specific emissions, without



**Figure 13.** LCA results (ReCiPe H/A) in terms of single score representation for different impact categories: (a) midpoint level and (b) endpoint level.

considering the improvement at the expenses of the actual environmental impact.

## Conclusions

In this paper, two waste solvent technologies were studied as alternatives to the disposal by incineration of spent acetone-water mixtures from the pharmaceutical industry.

In the first alternative, a batch rectifier is used to concentrate the waste in order to obtain a distillate with a higher calorific value, which is then sent to off-site incineration either in a cement kiln (Alternative A11)

or in a conventional waste solvent incinerator (WSI, Alternative A12). With the aim to recycle on-site the dehydrated solvent, a hybrid process composed by a rectifier followed by a pervaporation unit, both of them operated in batchwise mode was also studied. Here, four scenarios were considered, comprising two kinds of membrane materials and two different vacuum systems.

For each alternative, the conceptual design was carried out with the aid of conceptual models of the unit operations involved. While the minimum energy demand of each distillation task was calculated resorting to pinch theory,<sup>[11]</sup> a new algorithm to estimate the

minimum membrane area of a pervaporation task was presented in Section 2.3.1. Based in the improved memory method,<sup>[44]</sup> the number of dynamic simulations of the system feed tank- membrane unit is maintained at its minimum value. It is noteworthy that the overall balance of the membrane task and its corresponding area requirement can be calculated in advance even when the distillation task design is not still accomplished. While the minimum membrane area for the HybSi membrane from Pervatech was 7.6 m<sup>2</sup>, about 200 m<sup>2</sup> were required for the polymeric membrane studied in Ray & Ray.<sup>[17]</sup> This large difference in the area requirement is mainly due to the difference in flux and selectivity to achieve the desired separation requirements. Consequently, the high values for the membrane area and the permeate amount will require an expensive process that discourages the use of the polymeric membrane for acetone recovery at least at the operating conditions studied.

Rigorous simulations of the distillation tasks with Aspen Batch Distillation<sup>[29]</sup> were also performed to validate the results at the conceptual model level and to include the hold-up issue. Results obtained by rigorous simulation were almost coincident with those obtained from the conceptual model. While the maximum relative error in the steam consumption was about 15%, a relative error as low as 8% was achieved in the cooling water requirement. From the conceptual model, it was concluded that the energy requirement of the distillation task corresponding to the hybrid process with the ceramic membrane unit coupled to a vacuum pump/refrigeration system (Alternative A21) was only 4.5% above the corresponding to the standalone processes (Alternatives A11 and A12) since the recycled permeate amount from the ceramic membrane is rather low.

Quasi-optimal values for design and operation variables were used as input data to perform the economic assessment of each alternative. From the analysis of the economic figures, it was concluded that solvent recovery through the hybrid process using a steam-jet ejector system for vacuum production (Alternative A22, 597 U \$\$/ton) is the better option mainly due to the savings in the cost of fresh solvent (about 850 U \$\$/ton).

LCA was applied to evaluate the environmental impact of both alternatives. Optimal values for the utilities, that is, cooling water, electricity, and steam needed for distillation and pervaporation were used as the input data to perform the environmental analysis with LCA. From the environmental analysis, two main conclusions can be drawn: i) the use of the distillate as an alternative fuel in a cement kiln leads to a reduction in emissions that is relevant for human health and ecosystem quality and, ii) in terms of depleted resources, the hybrid process distillation/pervaporation

with the ceramic membrane HybSi from Pervatech (Alternative A21, 625 U \$\$/ton) shows the lowest impact due to the solvent recovery. Given the minimal difference in the overall costs between Alternatives A21 and A22, we adopted the hybrid process coupled to a vacuum pump/refrigeration system (Alternative A21) as the more suitable treatment technology. This alternative shows not only a significant economic benefit but also a low environmental impact, therefore both aspects encourage the implementation of this technology instead of the conventional waste solvent incineration.

## Nomenclature

A	Acetone, treatment alternative
$a_{min}^*$	Minimum membrane area for the base case
$A_{min}^*$	Minimum membrane area for the actual design
$B1_{\alpha}$	Still content at the beginning of the first cut
$B1_{\omega}$	Still content at the end of the first cut
$B2_{\alpha}$	Still content at the beginning of the second cut
$2_{\omega}$	Still content at the end of the second cut, Residue <sub>2</sub> = $B2_{\omega}$
$B3_{\alpha}$	Product vessel content at the beginning of the membrane operation
$B3_{\omega}$	Product vessel content at the end of the membrane operation, Product = $B3_{\omega}$
Cut <sub>1</sub>	Distillation task, first cut
Cut <sub>2</sub>	Distillation task, second cut
$D$	Distillate flow rate (kmol/h)
$F$	Fresh feed amount (kmol)
$I$	Environmental impact
$M_0$	Batch size (kmol)
$P$	Permeate amount (kmol)
R, 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)
W	Water
$x_i^B$	Instantaneous mole fraction of component $i$ in the still, initial value
$x_B$	Vector of instantaneous still compositions
$x_D$	Vector of instantaneous distillate compositions
$x_i^D$	Instantaneous mole fraction of component $i$ in the distillate

## Greek letters

$\eta$	Rectification advance defined as the ratio between the overall amount of product (kmol) recovered as distillate and the initial still holdup (kmol)
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$\sigma_i^D$  Fractional recovery of component  $i$  in the distillate  
 $\Delta I$  Environmental impact change

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