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Ethanol Production from Corn Contaminated with Fumonisins: A Preliminary Economic Analysis Including Novel Processing Alternatives

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Supporting Information

ABSTRACT: In this work, technical and economical feasibility of bioethanol production from corn with high concentrations of fumonisins is analyzed. Based on data obtained from a limited number of experiments, the cost data of ethanol facilities and conceptual design methods maximum prices for corn contaminated with fumonisins are estimated. The scope of the analysis includes average ethanol concentrations in the fermentor in a range of 6 wt % and 3 wt % for noncontaminated corn and strongly contaminated corn (1400 ppm), respectively. The maximum price for contaminated corn varies from 66% to 33% of the fumonisins-free feedstock cost, according to the level of contamination. The performance of the continuously operated process was also analyzed considering the coupling of the fermentor with a pervaporation unit for continuous ethanol separation. Estimations were made for a volumetric productivity of alcohol of 7.8 kg/(m^3 h) and membrane flux (0.9 kg/(m^2 h)) and selectivity (S = 5) corresponding to a commercial PDMS membrane for a level of 6 wt % ethanol in the stirred-tank fermentor. Results show that an increase of 100% in the membrane flux with a constant value for the selectivity is required to make the continuous alternative attractive.

1. INTRODUCTION

Concerns about global warming, depletion of fossil fuels, and security of energy supply have increased interest in more-sustainable energy sources.[1] This is especially true in the transport sector, because of its significant contribution to greenhouse gas (GHG) emissions, the impact of which will continue to increase in the future.[2] Bioethanol, or ethanol derived from biomass, has been recognized as a potential alternative to petroleum-based transportation fossil fuels.[3] Therefore, worldwide countries are interested in developing and expanding their biofuel market. As a consequence, the world bioethanol production has increased from ~14.8×10^9 L in 2005 to more than 56.4×10^9 L in 2012.

Ethanol can be obtained via the common fermentation process with *Saccharomyces cerevisiae* yeast. Raw materials for fermentations include a variety of feedstocks, which are subdivided into three main groups: molasses, starchy materials, and lignocellulosic materials. Except for molasses, the last two require a hydrolysis and saccharification treatment in order to obtain a high yield of fermentable sugars and release the essential nutrients from the feedstock, which are utterly important for the performance of the yeast.

Corn is one of the most popular raw materials for the industrial production of bioethanol and is the most used starchy raw materials in the United States.[4,5] Two distinct processes for processing corn are common, i.e., wet milling and dry milling. The corn wet milling process is designed to efficiently separate various products and parts of shelled corn for various food and industrial uses. The primary products of the corn wet milling process include corn starch and edible corn oil. On average, a bushel of corn weighs 25.4 kg at 10% moisture and through the wet milling process it produces 14.3 kg of corn starch, 5.7 kg of corn gluten feed, 1.1 kg of corn gluten meal, and 0.7 kg of corn oil.[6] The starch is further used to produce ethanol. Water and enzymes must be added and usually not all the starch can be used for ethanol production, so some of the syrup ends up becoming high-fructose corn syrup, which is a common and inexpensive sweetener.

Through the corn dry milling process, a bushel of corn typically produces 10.2 L of ethanol, 8.2 kg of distillers dried grains with soluble (DDGS), and 8.2 kg of CO_2.[6] After milling, the unit operations in dry milled corn processing include gelatinization (cooking) of starch, enzymatic liquefaction and saccharification to fermentable sugars, and fermentation of sugars by yeast.[7] The byproducts of this fermentation process are wet distillers grains (WDG) and thin stillage, which is also called distillers soluble (DS). WDG is made of coarse grain particles while the thin stillage contains yeast cells, soluble nutrients, and very small grain particles.

The advantages of the wet milling process over the dry milling process are easy to see with so many byproducts that can be sold to compensate for the cost of the process. However, much of the machinery is more expensive than that involved in the dry milling process. The two most common versions of distillers grains consumed by the livestock are WDG and

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DDGS. WDG contains primarily unfermented grain residues (protein, fiber, fat) and up to 70% moisture; it has a shelf life of 4−5 days and involves the transport of 70 wt % water. WDG supply transport is economically viable usually within a radius of 200 km from the ethanol production facility. DDGS is WDG that has been dried with the concentrated thin stillage to 10%−12% moisture; it has an almost indefinite shelf life and may be sold and shipped to any market, regardless of its vicinity to an ethanol plant. Of course, drying is costly, because it requires the input of energy.[8]

One of the biggest issues regarding grain crops is that they can become infected with fungi prior to harvest and during storage. Even though the use of fungicides is a common activity that aims to minimize fungal infection in corn and other cereals, the efficiency of this prophylactic measurement presents a strong dependence on the environmental conditions. Thus, although the contamination of the plant can be minimized, a healthy crop can never be assured. Corn kernels are subject to infection by a variety of toxigenic fungi, most commonly *Aspergillus flavus*, *Fusarium verticillioides* (syn. *F. moniliforme*), and *F. proliferatum*.[9] Some of significant importance are the *Fusarium* fungi that produce several mycotoxins, the most important of which, from the point of view of animal health and productivity, are the trichothecenes, zearalenone, moniliformin, and the fumonisins.[10] Since *F. verticilloides* infects maize worldwide, it is not surprising to find that fumonisins contaminate maize from every geographic region tested to date.[11] The natural occurrence of fumonisins (FB_1, FB_2, and FB_3) has been reported in commercial corn and/or corn-based feeds and foods from Argentina, Australia, Brazil, Botswana, Bulgaria, Canada, China, Egypt, France, Italy, Japan, Kenya, Hungary, Nepal, Peru, South Africa, Switzerland, the United States, and Zimbabwe.[10−13] Studies made by the Argentinean National Institute of Agricultural Technology (INTA) have shown that the variability in the concentrations of fumonisins in naturally contaminated corn goes from 5.2 ppm up to 154.4 ppm.[14] Natural contamination of corn with *Fusarium* fungus depends mostly on the environmental conditions presented during and after the harvest; consequently, a wide range of fumonisins concentrations can be expected. Chulze et al.[15] found that the production capacity of *Fusarium verticillioides* isolates from Argentina, when growth on a corn substrate, increased from 10 ppm to 3990 ppm. The values presented by Gallardo-Reyes et al.[16] for isolates of the same fungus found in Mexico increased from 500 ppm to 4893 ppm.

The risk of fumonisins to human and animal health prompted the United States Food and Drug Administration (USDA) to propose a guideline to allow a maximum mycotoxin content of 2 ppm in corn and corn products for human consumption.[9]

The contamination with *F. verticilloides* produces changes in the nutritional content of the corn, and, when the contamination reaches an advanced stage, the corn is visibly darker and presents the typical rotten state. This corn, which usually has a high concentration of fumonisins, is not acceptable for animal or human food, representing considerable money lost for the farmer. A practical strategy for salvaging fumonisin-contaminated grain and screenings, both of which tend to contain high levels of fumonisins, is the production of ethanol fuel.[17] Kłosowski and Mikulski[18] studied the influence exerted by the presence of fumonisins on alcoholic fermentation indicators—namely, alcohol concentration, productivity, yield and energy, using contaminated-with-fumonisins corn as raw material—and saw no significant differences with the control lot. However, the concentration used in their experiences is much lower than the values reported by Presello et al.[14]

Little degradation of fumonisins occurs during fermentation, and most studies show that the original mycotoxin content remains largely intact in the other fractions, including WDG and other fractions usually combined into DDGS, or other livestock feed coproducts. However, these toxins are not found in distilled ethanol. Bothast et al.[17] reported that 85% of the fumonisin B1 in the starting corn was recovered mostly in the DDG, and DS. Wu and Munkvold[19] estimated current losses to the swine industry from weight gain reduction due to fumonisins in added DDGS, but it is difficult to estimate what the economic impact would be on ethanol producers when using a low-quality corn.

Another issue in bioethanol production is the fermentation inhibition by the ethanol product itself and as a consequence, rather low ethanol concentrations are reached in the final fermentation broths.[20] A two-stage distillation train, followed by a dehydration step, is commonly used to purify the ethanol of the fermentation broth. Nevertheless, using distillation as the first purification step after the fermentation operation has some disadvantages. These include batch operation of the fermentor, low glucose-to-ethanol yield, no reuse of salts and microorganisms, and high energy demands.[20] In this field, a renewed interest in exploring the alternative given by a continuous process occurs.[4,21]

In this work, two main objectives for bioethanol production are examined: (i) the feasibility of using strongly contaminated corn as feedstock, and (ii) the coupling of a hydrophobic pervaporation membrane to the fermentor to switch the operation of the fermentor from batchwise to continuous operation.

To cope with the first objective, a preliminary economic analysis is performed in order to estimate the maximum price for corn contaminated with fumonisins. This task is intended to aid both the ethanol producer, by establishing a maximum price for contaminated feedstock, and the corn grower, by diminishing losses due to a feedstock that otherwise should be discarded.

To switch the operation mode of the fermentor, replacing the first distillation column by a pervaporation unit seems a very promising technology.[4,22] This is because a pervaporation unit coupled to a fermentor will selectively remove ethanol from the broth, hence keeping the ethanol concentration below inhibitory levels for the microorganisms and increasing the ethanol yield in the fermentation step. Furthermore, pervaporation has inherent advantages over alternative technologies due to the simplicity of operation, the absence of extra chemicals, low energy requirements, and, hence, low operational cost. Therefore, a preliminary economic analysis embracing all process steps will allow determination of the chance of success of this alternative and at the same time, address future research needs.

2. APPROACH

In this contribution, we developed a process and cost model for both conventional and hybrid processing facilities producing 24 × 10^6 L/yr of bioethanol from corn. The approach considers three sources of data: (i) cost data of ethanol facilities, (ii) data from a limited set of experiments, and (iii) data from

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conceptual modeling techniques for those processes for which information is scarce.

Cost Data of Ethanol Facilities. We mainly used the data from Kwiatkowski et al.[23] and Hoch and Espinosa.[24] The first contribution contains relevant information gathered from ethanol producers, technology suppliers, equipment manufacturers, and engineers working in the industry; it was focused on evaluating bioethanol production from corn. The second paper supplies data for the purification process through hybrid technologies such as distillation plus extractive distillation and distillation plus pervaporation with hydrophilic membranes. Investment costs were adjusted through the use of equipment/cost scaling factors and updated to 2011 using the factor CEPCI/400, where CEPCI is the updated Chemical Engineering Plant Cost Index. See Appendix A in the work by Hoch and Espinosa[24] for details of the cost model corresponding to the purification plant.

Equipment Performance from Experimental Runs. In order to allow the calculation of the volume of the fermentation sector and the membrane area for the hydrophobic pervaporation sector, experimental runs were performed.

Several fermentation experiments at 30 °C were performed with six different concentrations of corn contaminated with fumonisins (*Fusarium verticillioides*) obtained by mixing free-of-contamination maize with strongly contaminated corn (1400 ppm). Strain No. 5 of *Saccharomyces cerevisiae* of the "Universidad Nacional del Litoral, UNL" was employed. Figure 1 shows the appearance of the corn used in this study prior to

Figure 1. Appearance of noncontaminated (left) and strongly contaminated (right, 1400 ppm) maize.

and after the contamination. Figure 2 shows the final concentration of ethanol achieved in these experiments (see the work of Sosa et al.[25] and Ricca[26]).

As can be seen from Figure 2, the final ethanol concentration in the fermentation broth takes values from 6 wt % for the case of free of fumonisins corn to ~3 wt % for strongly contaminated corn. Based on the data above and a residence time of 64 h, plant designs corresponding to final ethanol concentrations of alcohol in the fermentor of 6, 5, 4, and 3 wt % were calculated.

In the analysis of the fermentor plus hydrophobic pervaporation alternative, we performed a bibliographic search to estimate a value for the fermentor volumetric productivity. O'Brien and Craig[27] obtained values of ~7.8 kg/(m^3 h) for stationary values of the alcohol concentration of ~6 wt %. Therefore, we took this value to size the fermentor in the continuous process. Note that, to analyze the continuous

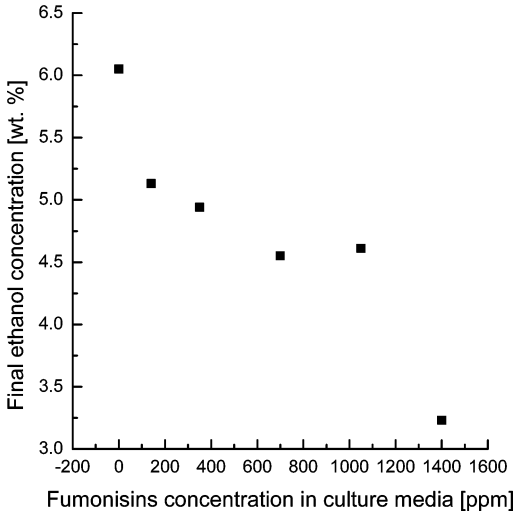

Figure 2. Final ethanol concentration (wt %) versus fumonisins concentration in the culture media (ppm).

alternative, we only considered the base case of bioethanol production from noncontaminated maize.

Since a continuous process requires the continuous removal of alcohol from the fermentation broth, pervaporation experiments with a commercial PDMS membrane were carried out at 30 °C and a vacuum level of <3 mbar. Details of the experimental procedure can be found in Chovau et al.[21]

Figures 3 and 4 show the ethanol flux and the overall permeate flux versus the ethanol concentration (wt %) in the

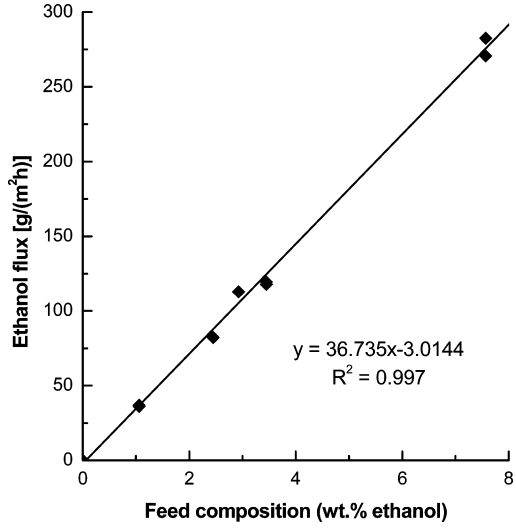

Figure 3. Ethanol flux in the permeate versus feed composition. Commercial PDMS membrane.

retentate. A membrane flux of 0.9 kg/(m^2 h) and a selectivity value (S) of 5, which corresponds to an alcohol level of 6 wt % in the stirred-tank fermentor, is selected to size the membrane unit.

Design of the Purification Process with the Aid of Conceptual Modeling Techniques. The design of optimal separation flowsheets for multicomponent mixtures is still not a solved problem. This is especially the case when nonideal or azeotropic mixtures or hybrid separation processes are taken into account. Marquardt et al.[28] reviewed recent developments

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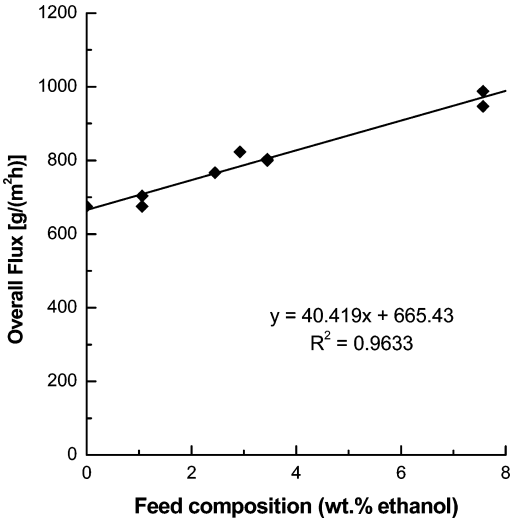

Figure 4. Overall flux in the permeate versus feed composition. Commercial PDMS membrane.

in this field and presented a systematic framework for the design of separation flowsheets. This framework proposed a three-step approach. In the first step, different flowsheets are generated. In the second step, these alternative flowsheet structures are evaluated with shortcut methods. In a third step, a rigorous MINLP optimization of the entire flowsheet is executed to determine the best alternative.

Since several alternative flowsheets have already been eliminated, only a few optimization runs are necessary in this final step.

Following the ideas of Marquardt, two alternative flowsheets were generated in the work of Hoch and Espinosa,[24] and, based on the results obtained, it was decided to explore the alternative that studies distillation plus hydrophilic pervaporation while discarding the purification via distillation plus extractive distillation.

In this contribution, the approach selected for the third step avoids the MINLP optimization since, for this problem, it is possible to determine, for a given specification of the distillate composition (main column), a sequence of evaluation steps that allow us to address the entire process without iteration. By varying this degree of freedom, it is possible to determine the optimal flowsheet. For a given value of the distillate composition, each unit operation in the sequence is first designed with the aid of a conceptual model and then a rigorous simulation in Aspen+[29] is performed to refine results. The corresponding economic figures then can be calculated from cost models of the unit operations. Thus, the tradeoff between distillation and membrane costs is assessed by parametrically varying the distillate composition of the main column. A final refinement of results for the optimal flowsheet is also performed with the aid of Aspen+.

It is noteworthy that when the flowsheet becomes more complex, it might be difficult to determine a sequence of evaluation steps, even if it exists. In such a case, a rigorous MINLP optimization of the entire flowsheet must be executed to determine the best alternative.[28,30]

To cope with the problem of maize contaminated with fumonisins, optimal purification flowsheets corresponding to end ethanol concentrations in the fermentor of 6, 5, 4, and 3 wt % are obtained. Only one optimal flowsheet, without the beer column, is obtained for the continuously operated process (6 wt % ethanol). In all cases, the optimization variable is the mole fraction of ethanol in the distillate stream of the main column.

3. PROCESS OPTIMIZATION FOR HOT WINES CONTAINING DIFFERENT AMOUNTS OF ETHANOL

Process Description. The influence of ethanol concentration on the cost of the purification step was assessed through optimization of a hybrid process consisting of a beer column, a main column, and a pervaporation unit. For the sake of simplicity, it was assumed that the hot wine is a binary mixture of ethanol and water. This assumption is valid whenever both the azeotropic composition and tangent pinch points that control the separation are taken into account through an appropriate activity model for the liquid phase, such as Wilson or NRTL. Note, however, that it should be removed for a detailed design of an actual process.

While the first column (known as the "beer column") separates the solids and most of the water from a vapor stream composed of ethanol and water, the main distillation column produces a bottom stream composed of nearly pure water (<0.2 wt % ethanol) and a distillate stream with a composition near that of the ethanol−water azeotrope. The distillate stream is further processed in the hydrophilic pervaporation sector to achieve a high-purity retentate stream (>99.8% wt % ethanol) and a permeate stream that is recycled to the main column. The pervaporation task is evaluated from the model proposed by Vier[31] and Bausa and Marquardt[30] for the polymeric composite membrane PVA/PAN MOL 1140 (GFT, Germany). The plant capacity is 24×10^6 L/yr of bioethanol.

Optimization Strategy. Optimization of the entire plant is a very challenging task, because of the nonidealities of the ethanol−water binary mixture and the complexity of the plant. However, a quasi-optimum design is still feasible to be obtained by decomposing the plant into the beer column and the hybrid process distillation plus pervaporation. Hoch and Espinosa[24] demonstrated that is possible to operate the beer column near its minimum energy demand. Furthermore, Bausa and Marquardt[30] and Sosa and Espinosa[32] established a procedure to optimize the separation of azeotropic binary mixtures via distillation plus pervaporation. In this case, the optimization variable is the distillate composition.

The optimization procedure intensively uses both conceptual and rigorous models for the design and simulation of each unit operation comprising the hybrid process. While the conceptual models for distillation columns resort to pinch theory (see the work of Doherty and Malone[33]), which leads first to the calculation of the minimum energy demand and then to the estimation of the number of stages via the well-known McCabe Thiele method, the membrane unit performance is obtained by integrating the rigorous mass-transfer model for the commercial membrane PVA/PAN MOL 1140 (from GFT, Germany). However, as suggested by Bausa and Marquardt,[30] the model integration is done by considering the maximum driving force (i.e., no liquid temperature drop) at each volume element to obtain the minimum membrane area needed for separation. Actual membrane area is approximated by multiplying the minimum membrane area by a fixed factor of 1.25. In all cases, results from the conceptual model level are refined in the rigorous simulation level with the aid of Aspen+.

Equipment Design from Conceptual Models and Rigorous Simulation. *Beer Column.* The vapor stream leaving the stripping column captures nearly all of the ethanol

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and components in traces produced during the fermentation step. The minimum energy demand of the process (i.e., minimum reboiling ratio) is calculated through the lever arm rule by setting the bottom product as high-purity water and allowing the composition of the vapor stream to correspond to the vapor in equilibrium with hot wine. In other words, a pinch at the top of the stripping column is considered. In order to obtain a feasible design, the following steps are performed:

(i) Determine the maximum feasible separation and minimum energy demand (s_{min}) by applying pinch theory. For this task, an equilibrium calculation that can be performed in a conceptual model framework (such as DISTIL) is required;[34]
(ii) Calculate the reboil ratio, $s = 1.2s_{min}$;
(iii) Set a value for the number of stages $N_{stages}^{beer\ col}$;
(iv) Simulate a stripping column with the reboiler first and then replace the reboiler with steam, taking into account the reboiler duty and the latent heat of condensation of steam. This task can be done in a simulation framework such as Aspen+.

Table 1 shows the "limiting" compositions of the streams entering and leaving the stripping column, together with the minimum value of the reboiling ratio (s_{min}). Since the vapor stream leaving the stripping column is assumed to be in equilibrium with the hot wine, an infinite number of stages are required to perform the separation.

Table 1. Overall Mass Balance and Energy Demand of a Beer Column with an Infinite Number of Stages (DISTIL)[a]

component	$x_{HOT\ WINE}$	$y^*_{HOT\ WINE}$	x_W
ethanol	0.0243521	0.205391	0
water	0.9756479	0.794609	1

$$s_{min} = \frac{(x_W - x_{HOT\ WINE})}{(x_{HOT\ WINE} - y^*_{HOT\ WINE})} = 0.1345$$

[a]The hot wine contains 6 wt % ethanol.

Theoretically, s_{min} represents the minimum energy demand for which pure water is obtained at the bottom of the column with a pinch at the top of the column. Reboiling ratios above s_{min} lead to a jump of the pinch region from the top to the bottom and, hence, pure water remains as the product at the bottom of the column. However, an increase in the water amount in the distillate is enforced, decreasing the separation power of the beer column. On the other hand, for reboiling ratios below the "minimum", the pinch is still located at the top of the column, but alcohol is lost in the bottom product. Figure 5 schematically shows how products of a column with an infinite number of stages move along the mass balance line as the actual reboiling ratio s takes values above or below the "minimum".

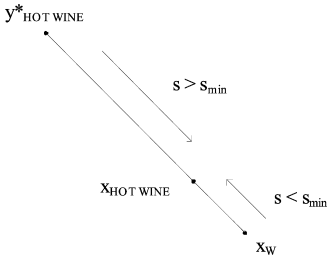

Figure 5. Influence of actual reboiling ratio (s) on the products of a column with an infinite number of separation stages.

Bearing in mind the ideas above, operation of the beer column as close as possible to s_{min} is preferred for two reasons: first, the energy demand of the process approaches its minimum value, and second, the amount of water withdrawn from the hot wine tends toward its maximum value.

A quasi-optimal column design was achieved, with 20 equilibrium stages, a column diameter of 1.219 m and a reboiler duty of 3337 kW. A vaporization enthalpy of ΔH_{vap} = 39560 kJ/kmol is used to relate reboiler duty with live steam heat duty, which, for the sake of simplicity, is referred to as Q_{reb}. The composition of ethanol in the outlet stream is ~37 wt %, and it well approaches the equilibrium value.

Main Column. The feed to the main column is composed of the vapor outlet stream from the beer column and the condensed permeate stream from the pervaporation sector. Input data to the conceptual model are as follows: (i) the mole fraction and the fraction of liquid of the mixed stream, (ii) the distillate mole fraction (optimization variable), and (iii) the mole fraction of the water-rich bottom stream.

For the sake of simplicity, a one-feed column is considered. The conceptual design is performed in the conceptual modeling framework of DISTIL, which considers the occurrence of both feed pinches and tangent pinch points. Output data from the conceptual model are the minimum reflux ratio (R_{min}), the operation reflux ratio ($R_{op}^{Main\ col} = 1.05R_{min}$), and the actual number of stages ($N_{stages}^{Main\ col}$). Once the initial design is obtained, a rigorous simulation in Aspen+ is carried out. Table 2 shows the operating and design variables for the main distillation column calculated from DISTIL and Aspen+ for the optimal distillate mole fraction corresponding to a plant processing a feed containing 6 wt % ethanol. A quasi-optimal column design was achieved, with 19 equilibrium stages, a column diameter of 1.372 m, a condenser duty of 3586 kW, and a reboiler duty of 425.7 kW.

Table 2. Overall Mass Balance and Operating and Design Variables for the Main Column[a]

Overall Mass Balance			
	$x_{feed}^{Main\ col}$	x_D	x_B
ethanol	0.17899	**0.80000**	0.0001
water	0.82102	0.20000	0.9999
liq. fraction	0.04462	1.00000	1.0000

Operating and Design Variables				
	R_{min}	$R_{op}^{Main\ col}$	feed stage	$N_{stages}^{Main\ col}$
DISTIL	3.717	3.90	9	19
Aspen+		4.10	9	19

[a]The hot wine contains 6 wt % of ethanol. The feed to the main column is a mixture between the vapor stream leaving the beer column and the condensed permeate stream from the pervaporation sector.

Pervaporation. A conceptual design of pervaporation for the polymeric composite membrane PVA/PAN MOL 1140 (GFT, Germany), following the model proposed by Vier[31] and Bausa and Marquardt,[30] was implemented in a Delphi environment[35] to determine the minimum membrane at 90 °C and 2.026 kPa. Under these conditions, a maximum permeate flux of 1.125 kg/(m^2 h) is obtained. Model equations and parameters used are reported in the Supporting Information of this manuscript.

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Figure 6 shows both the permeate composition and vapor composition versus water mole fraction. It is clear that

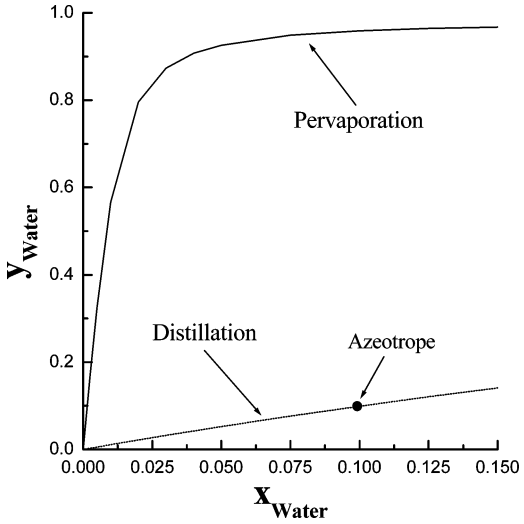

Figure 6. Comparison between separation performance of pervaporation at 90 °C and 2.026 kPa, and distillation at 101.3 kPa.

pervaporation allows one to overcome the azeotropic composition. Therefore, distillation followed by a pervaporation unit is appropriate to obtain high-purity ethanol.

In the typical plate and frame 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.[36]

Bausa and Marquardt[30] 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 until the composition of the product in the retentate achieves the specified value. The actual membrane area is approximated by multiplying the minimum membrane area with a fixed factor of 1.25.

Since the feed flow rate $F^* = D$ of a given alternative is unknown, integration of the model from known values of the retentate flow rate R and composition x_R must be performed in the following way:

(i) Integrate the mass-transfer model (from Vier[31]) for a normalized value of the feed flow rate ($f^* = 1$ kmol/h) with mole fraction $x_F^* = x_D$ (optimization variable), until the retentate composition x_R specified at the design level is achieved;

(ii) Calculate the values of the minimum membrane area $A_{\text{memb}}^{\min}$, feed flow rate $F^* = D$, and permeate flow rate P from normalized values of the area $a_{\text{memb}}^{\min}$ and retentate flow rate r obtained in step (i), and the retentate flow rate R calculated from the mass balance around the entire process:

$$A_{\text{memb}}^{\min} = \left(\frac{R}{r}\right) a_{\text{memb}}^{\min} \tag{1}$$

$$P = \frac{R}{r}(1 - r) \tag{2}$$

$$F^* = D = \frac{R}{r} \tag{3}$$

Hence, a minimum membrane area can be calculated for a given value of the optimization variable $x_F^* = x_D$.

The model was also simulated in Aspen+ as a user operation extension. To this end, the model was first written in the Aspen + Custom Modeler and then exported to Aspen+. A membrane area of 813 m^2 is needed for an optimization variable value of 0.8.

Calculation Sequence and Results. Taking into account that the entire plant mass balance can be calculated from given values of the retentate mole fraction (99.8 wt % ethanol) and, the ethanol mole fraction in the bottom of the main column (0.02 wt %) and the corresponding value in the bottom of the beer column (0.00 wt %), a degree-of-freedom analysis shows that one degree of freedom remains unspecified. We select the composition x_F^* of the feed to the membrane unit, which, in turn, is the distillate composition of the main column; i.e., $x_F^* = x_D$.

For a given value of the optimization variable, optimal values for operating and design variables of each unit operation are obtained from the following calculation sequence without the

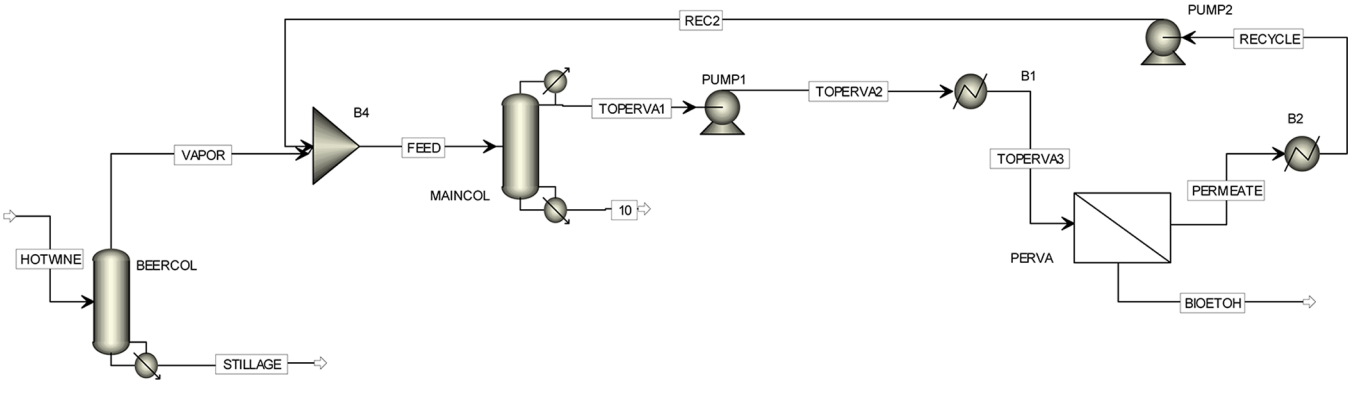

Figure 7. Hybrid purification process in Aspen+.

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need to iterate: (i) beer column, (ii) membrane unit, (iii) mixing operation, and (iv) main column. Note that steps (ii), (iii), and (iv) can be repeated for different values of the distillate mole fraction until the value of the global optimum is found. For this case, simulation of the entire flowsheet is done in order to refine the results (see Figure 7).

Figure 8 shows the results obtained for the base case. A minimum in the purification cost is achieved for a mole fraction of ethanol in the distillate stream of the main distillation column of 0.8.

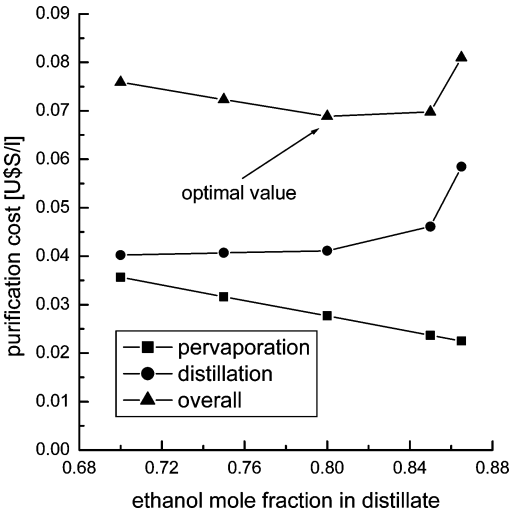

Figure 8. Optimal distillate composition for the base case (6 wt % ethanol in the hot wine).

A similar approach can be followed for the other hot wine compositions. Investment costs are approximately 0.023 U$S/L (U$S/L denotes U.S. dollars per liter) and are almost independent of the composition of the hot wine, because the increase in the investment necessary in the distillation units as the alcohol concentration in the hot wine diminishes is compensated by a decrease in the membrane area needed to perform the separation. In other words, the optimal distillate value approaches the azeotropic composition as the composition of ethanol in the feed to the process diminishes its value, with respect to the base case. The operating costs, on the other hand, are strongly dependent on the feed composition. Costs of 0.046 and 0.070 U$S/L are expected for a feed containing 6 and 3 wt % alcohol, respectively. The corresponding overall energy demands in the reboilers are 3763 and 6428 kW, respectively.

It is noteworthy that, for the case of the hybrid process fermentor plus hydrophobic pervaporation, the feed to the process is 24 wt %. In addition, the beer column is removed from the flowsheet. A quasi-optimal column design was achieved, with 27 equilibrium stages, a column diameter of 0.9144 m, a condenser duty of 1526 kW, and a reboiler duty of 1623 kW. As expected, both investment costs (0.021 U$S/L) and operating costs (0.0248 U$S/L) are lower than the costs corresponding to the state-of-the-art process (Figure 8).

Finally, note that the same results, in terms of energy demand, could have been achieved by considering only one column in the state-of-the-art alternative, because only the main components of the mixture were considered in the analysis. However, considering the two columns allows the designer to include the influence of trace components on the distillation train design and apply different cost functions to each column.

4. OVERALL RESULTS

Estimation of the Maximum Price for Contaminated Corn. In order to estimate the maximum feasible price for contaminated corn, we follow the procedure below:

- Design a plant for the base case (6 wt % ethanol, 0 ppm), annual production = 24×10^6 L,
- Calculate the production cost for the base case in U.S. dollars per liter (i.e., 0.54 U$S/L),
- Design a hypothetic plant from corn with a given degree of contamination (i.e., 1400 ppm; 3 wt % ethanol),
- Calculate the maximum price, in units of U$S/L, as 0.54 − operation costs (i.e., 3 wt %) − investment costs (i.e., 3 wt %).

The overall production cost of 0.54 U$S/L for the base case is calculate by summing raw materials (78.5%), investment (23.7%), and operating costs (23.7%), and subtracting the

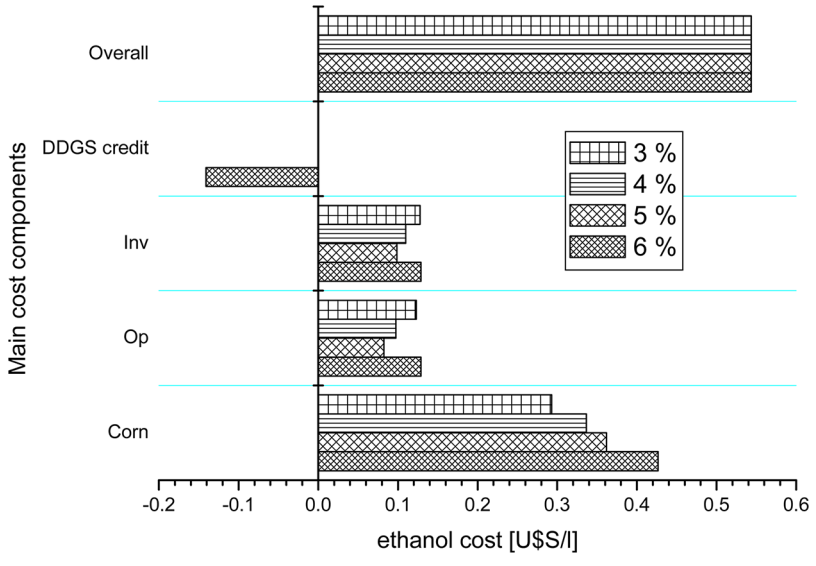

Figure 9. Ethanol cost versus main component costs for the base case and three hypothetical facilities.

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credit for the sale of coproducts (25.9%). Thus, the income from the sale of the DDGS equals the operating costs of the entire plant.

Figures 9−11 summarizes the results obtained for the base case and three processes departing from corn with different degrees of contamination. From the analysis of Figure 9, the following can be determined:

- The production cost is strongly influenced by the cost of corn, which amounts to 180 U$S/ton (2011 average) for the base case;
- Investment and operating costs for contaminated corn increase with decreasing final ethanol concentration in the fermentor (3−5 wt %);
- The investment and operating costs for the case of noncontaminated corn are slightly higher than those of contaminated maize, because the former includes the plant of DDGS; and
- Credit for the sale of the coproduct is only obtained for the case of uncontaminated corn, since, for the remainder, the contamination exceeds the allowable values.

Results shown in Figure 10 emphasize the loss in productivity produced by the use of contaminated feedstock.

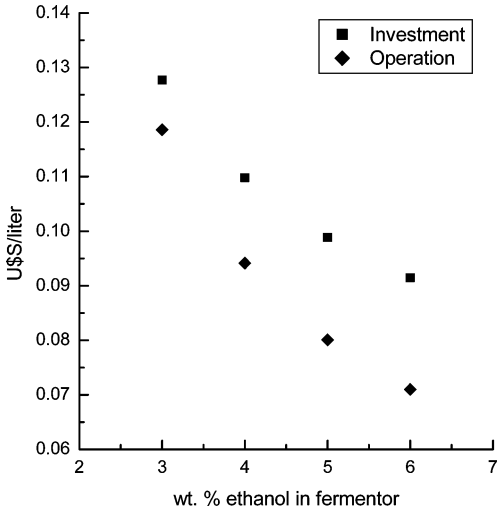

Figure 10. Influence of the final concentration of ethanol in the fermentor on investment and operating costs without considering the plant of DDGS.

Figure 11 presents the maximum price for the feedstock versus the alcohol mass fraction in the fermentor. Note that the corn price for the base case (without contaminating corn) is 180 U$S/ton (2011 average). For the remaining cases, it was calculated to obtain the same production cost than the base case. Thus, the values reported in Figure 11 can be interpreted as the maximum price that could be paid for grains with different degrees of contamination. The proposed metric takes into account the losses of productivity, considering both the operating costs and investment costs necessary to achieve the same annual amount of ethanol (i.e., 24×10^6 L/yr). Note, however, that, in practice, a mixture of noncontaminated corn with contaminated maize will be fed into the process.

Summarizing, the maximum price for maize that has been strongly contaminated (1400 ppm) is ∼33% of the price corresponding to noncontaminated corn. A contamination of

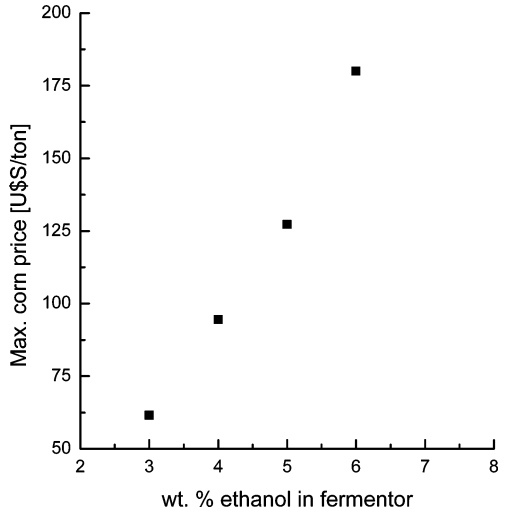

Figure 11. Maximum price per ton of corn versus the final concentration of ethanol in the fermentor for an annual production of 24×10^6 L of bioethanol.

∼140 ppm, on the other hand, allows a maximum price of ∼67% of that of the base case. This result is in agreement with the statement made by Kłosowski and Mikulski,[18] who concluded that no significant differences occur in fermentation indicators between noncontaminated and contaminated corn when considering low degrees of contamination.

Alternative Fermentor Plus Hydrophobic Pervaporation. Figure 12 shows the production cost breakdown for both the conventional alternative and the continuously operated process. The feed to the purification step is ∼24% ethanol by weight. Given the high requirement of membrane area (∼11 000 m^2), the costs of the hybrid alternative are more than ∼14% over the conventional alternative. Installation costs of the pervaporation sector were assumed to be 1500 U$S/$m^2$ with membrane replacement costs of 200 U$S/$m^2$ and a membrane lifetime of 3 years. The flux (0.9 kg/(m^2 h)) and selectivity (S = 5) of the commercial PDMS membrane tested were not sufficient to generate an attractive alternative. An increase of 100% in the membrane flux with a constant value for the selectivity would be expected to make the continuous alternative attractive.

5. CONCLUDING REMARKS

In this contribution, a design-based methodology is proposed to estimate the overall production and investment costs of bioethanol facilities. Relevant cost data from ethanol plants, a minimum set of experiments, and conceptual models of specific unit operations are key ingredients of the methodology.

Maximum feasible prices for grains with different degrees of contamination are obtained, taking into account inefficiencies in both operation and investment costs, with the aid of a methodology that is easy to apply for industry practitioners. Therefore, changes in the corn price can be handled properly. Maximum prices per ton for strongly contaminated feedstocks can achieve values as low as 30% of that of the noncontaminated maize.

The research approach was also applied to assess the feasibility of the alternative fermentor plus hydrophobic pervaporation. Given the flux and selectivity of the commercial PDMS membrane tested, production costs are 14% above that of the conventional alternative. An increase of 100% in the

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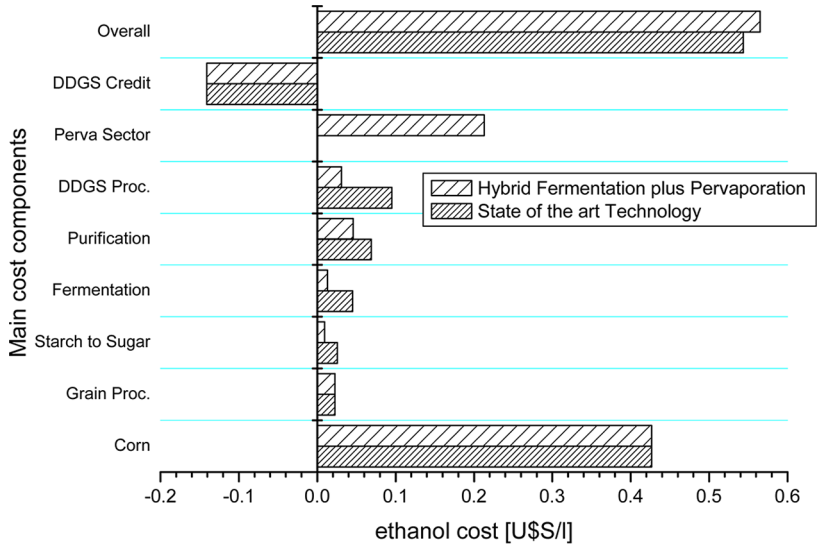

Figure 12. Ethanol production cost breakdown for both the conventional process and the continuously operated process.

membrane flux with a constant value for the selectivity would be expected to make the continuous alternative attractive.

Results obtained encourage studying the performance of the continuous process using process alternatives comprising both microfiltration and pervaporation membranes, together with yeast strains that are more tolerant to ethanol. Also, the influence of trace components on both the purification step design and the membrane operations performance are issues that deserve further research efforts.

■ ASSOCIATED CONTENT

Supporting Information

Equations and parameters for the mass-transfer model through the membrane PVA/PAN Mol 1140[30,31] are included in this section. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Lombardi, L. Life cycle assessment comparison of technical solutions for CO_2 emissions reduction in power generation. *Energy Convers. Manage.* **2003**, *44*, 93.

(2) Abrahamse, W.; Steg, L.; Gifford, R.; Vlek, C. Factors influencing car use for commuting and the intention to reduce it: A question of self-interest or morality? *Transp. Res., Part F* **2009**, *12* (4), 317.

(3) Govindaswamy, S.; Vane, L. M. Kinetics of growth and ethanol production on different carbon substrates using genetically engineered xylose-fermenting yeast. *Bioresour. Technol.* **2007**, *98*, 677.

(4) Vane, L. A review of pervaporation for product recovery from biomass fermentation processes. *J. Chem. Technol. Biotechnol.* **2005**, *80*, 603.

(5) Jacques, K. A.; Lyons, T. P.; Kelsall, D. R. *The Alcohol Textbook*, 4th Edition; Alltech, Inc.: Nottingham, U.K., 2009.

(6) O'Brien, D.; Woolverton, M. Updated trends in U.S. wet and dry corn milling production. In *AgMRC Renewable Energy Newsletter*, 2010. (Available via the Internet at http://www.agmrc.org/renewable_energy/ethanol/updated-trends-in-u-s-wet-and-dry-corn-milling-production/.)

(7) Jacques, K. A.; Lyons, T. P.; Kelsall, D. R. *The Alcohol Textbook*, 3rd Edition; Alltech, Inc.: Nottingham, U.K., 1999.

(8) Bonnardeaux, J. *Potential Uses for Distillers Grains*; Department of Agriculture and Food, Government of Western Australia: Perth WA, Australia, 2007.

(9) Boeira, L. S.; Bryce, J. H.; Stewart, G. G.; Flannigan, B. Influence of cultural conditions on sensitivity of brewing yeasts growth to Fusarium mycotoxins zearalenone, deoxynivalenol and fumonisin B1. *Int. Biodeterior. Biodegrad.* **2002**, *50*, 69.

(10) Placinta, C. M.; D'Mello, J. P. F.; Macdonald, A. M. C. A review of worldwide contamination of cereal grains and animal feed with Fusarium mycotoxins. *Anim. Feed Sci. Technol.* **1999**, *78*, 21.

(11) Munkvold, G. P.; Desjardins, A. E. Fumonisins in Maize: Can we reduce their occurrence? *Plant Dis.* **1997**, *81* (6), 556.

(12) Marasas, W. F. O. Fumonisins: Their implications for human and animal health. *Nat. Toxins* **1995**, *3* (4), 193.

(13) Sydenham, E. W.; Gelderblom, W. C. A.; Thiel, P. G.; Marasas, W. F. O. Evidence for the Natural Occurrence of Fumonisin B1, a Mycotoxin Produced by Fusarium moniliforme, in Corn. *J. Agric. Food Chem.* **1990**, *38*, 285.

(14) Presello, D. A.; Botta, G.; Iglesias, J.; Eyhérabide, G. H. Severity of fusarium ear rot and concentration of fumonisin in grain of Argentinean maize hybrids. *Crop Prot.* **2007**, *26*, 852.

(15) Chulze, S. N.; Ramirez, M. L.; Pascale, M.; Visconti, A. Fumonisin production by, and mating populations of, *Fusarium* section *Liseola* isolates from maize in Argentina. *Mycol Res.* **1998**, *102* (2), 141.

(16) Gallardo-Reyes, E.; Ibarra-Moreno, G. M.; Sánchez-Mariñez, R. I. *Rev. Mex. Fitopatología* **2006**, *24* (1), 27.

(17) Bothast, R. J.; Bennett, G. A.; Vancauwenberge, J. E.; Richard, J. L. Fate of Fumonisin B1 in Naturally Contaminated Corn during Ethanol Fermentation. *Appl. Environ. Microbiol.* **1992**, *58* (1), 233.

(18) Kłosowski, G.; Mikulski, D. The effect of raw material contamination with mycotoxins on the composition of alcoholic fermentation volatile by-products in raw spirits. *Bioresour. Technol.* **2010**, *101*, 9723.

(19) Wu, F.; Munkvold, G. P. Review: Mycotoxins in Ethanol Co-products: Modeling Economic Impacts on the Livestock Industry and Management Strategies. *J. Agric. Food Chem.* **2008**, *56*, 3900.
(20) Nomura, M.; Bin, T.; Nakao, S.-I. Selective ethanol extraction from fermentation broth using a silicalite membrane. *Sep. Purif. Technol.* **2002**, *27*, 59.
(21) Chovau, S.; Gaykawad, S.; Straathof, A. J. J.; Van der Bruggen, B. Influence of fermentation by-products on the purification of ethanol from water using pervaporation. *Bioresour. Technol.* **2011**, *102*, 1669.
(22) O'Brien, D. J.; Roth, L. H.; McAloon, A. J. Ethanol production by continuous fermentation−pervaporation: a preliminary economic analysis. *J. Membr. Sci.* **2000**, *166*, 105.
(23) Kwiatkowski, J. R.; McAloon, A. J.; Taylor, F.; Johnston, D. B. Modeling the process and costs of fuel ethanol production by the corn dry-grind process. *Ind. Crops Prod.* **2006**, *23*, 288.
(24) Hoch, P. M.; Espinosa, J. Conceptual Design and Simulation Tools Applied to the Evolutionary Optimization of a Bioethanol Purification Plant. *Ind. Eng. Chem. Res.* **2008**, *47* (19), 7381.
(25) Sosa, M. A.; Espinosa, J.; Basílico, J. C. Estudio de la viabilidad del maíz contaminado con fumonisinas como materia prima para la producción de bioetanol. In *XII Congreso Argentino de Micología y XXII Jornadas Argentinas de Micología*, Misiones, Argentina, 2011.
(26) Ricca, A. P. *Aprovechamiento de granos contaminados con fumonisina B1 para la obtención de etanol y análisis del posterior uso de las vinazas sólidas como complemento en alimento balanceado*. Ph. D. Thesis, Universidad Nacional del Litoral, Santa Fe, Argentina, 2006.
(27) O'Brien, D. J.; Craig, J. C., Jr. Ethanol production in a continuous fermentation/membrane pervaporation system. *Appl. Microbiol. Biotechnol.* **1996**, *44*, 699.
(28) Marquardt, W.; Kossack, S.; Krämer, K. A Framework for the systematic design of hybrid separation processes. *Chin. J. Chem. Eng.* **2008**, *16* (3), 333.
(29) *Aspen Plus V7.3 User Manual*, 2011.
(30) Bausa, J.; Marquardt, W. Shortcut Design Methods for Hybrid Membrane/Distillation Processes for the Separation of Nonideal Multicomponent Mixtures. *Ind. Eng. Chem. Res.* **2000**, *39*, 1658.
(31) Vier, J. Pervaporation azeotroper wässriger und rein organischer Stoffgemische-Verfahrensentwicklung und−integration, Ph.D. Thesis, Institut für Verfahrenstechnik, RWTH Aachen, Shaker Verlag, Aachen, Germany, 1995.
(32) Sosa, M. A.; Espinosa, J. Feasibility Analysis of Isopropanol Recovery by Hybrid Distillation/Pervaporation Process with the Aid of Conceptual Models. *Sep. Purif. Technol.* **2011**, *78*, 237.
(33) Doherty, M. F.; Malone, M. F. *Conceptual Design of Distillation Systems*, 1st Edition; McGraw−Hill Chemical Engineering Series; McGraw-Hill: New York, 2001.
(34) *Hysys & Distil User Manuals*; Hyprotech, Ltd.: Calgary, Canada, 1999.
(35) Borland Delphi 3; Copyright 1997 Borland International, Inc., Scotts Valley, CA.
(36) Melin, T.; Rautenbach, R. *Membranverfahren. Grundlagen edr Modul-und Anlagenauslegung*; VDI-Buch, Springer: Berlin/Heidelberg, Germany, 2007.