Paper 316a

Design of a Hybrid Distillation-Pervaporation Bio-Ethanol Purification Process Using Conceptual Design and Rigorous Simulation Tools

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Abstract

Optimization of both design and operation variables of a bio-ethanol purification plant intended to produce fuel grade ethanol is a challenge to make the bio-fuel a realistic alternative in the energy market.

In this work, we propose an evolutionary optimization procedure which intensively uses both conceptual and rigorous models for the design and simulation of unit operations involved in a bio-ethanol purification process. While conceptual models are used to determine initial values for design and operating variables of a given operation unit, rigorous simulation departing from initial estimates generated at conceptual design level enables to remove simplifying assumptions, interconnect equipments and calculate operating and investment costs.

Once an initial design of the purification plant is obtained, opportunities of improvement are easily recognized and then tested by performing the design and simulation steps until a cost-effective bio-ethanol purification plant is achieved.

Finding initial values for the column design is made easier within the conceptual design environment, which is used to obtain an initial estimation of the total number of trays of the main distillation column, placement of feed and side streams, and steam flow rate in the simulation environment. In addition, convergence of the rigorous model is enhanced by using initial estimates of internal profiles generated at the conceptual design level despite of the highly non-ideal behavior of the multicomponent azeotropic mixture.

The advantage of the method is that the systematic use of conceptual models allows the designer to capture the main characteristics of each operation involved in the process.

The main results obtained show a minimum in the operation costs corresponding to a minimum in the steam flow rate of the hybrid column. This minimum in steam flow rate can be only explained by the presence of the fusel component, which influences both the energy demand and feasible products of the hybrid column. Therefore, designs based on the binary system ethanol-water do not represent the system behavior in an accurate way. From this consideration emerges the importance of properly determining the amount of trace components that enter the purification process.

From the analysis of the results obtained it is also clear that the investment cost corresponding to the membrane sector is high enough to promote future research efforts in testing both selectivity and flux behavior of other commercial pervaporation membranes.

***Keywords**: Bio-ethanol Purification, Evolutionary Optimization, Conceptual Design, Rigorous Simulation.*

1. Introduction

There is great incentive in developing bio fuel processes, and optimization constitutes a tool that allows the improvement of process conditions and structure. Bio-ethanol produced from corn is a bio-fuel of interest, but the complexity of the production plant makes it difficult to propose a general superstructure taking into account all possibilities, and the high non-linearity of the corresponding models requires rigorous solution methods. In this work, we propose an evolutionary optimization procedure which uses intensively both conceptual and rigorous models for the design and simulation of unit operations.

The bio-ethanol purification plant comprises a separation sector with two distillation columns where both the reboilers are replaced by live steam feeds, a decanter and a pervaporation unit, used to obtain fuel grade ethanol. The plant is integrated with two other sectors, a fusel plant with several liquid-liquid separators, and an evaporation plant, where a triple effect evaporator, a centrifuge and a rotary dryer are used to obtain an animal feed co-product rich in proteins. Given the plant complexity and the high non-linearity of the corresponding models, we propose an evolutionary optimization procedure which uses intensively both conceptual and rigorous models for the design and simulation of unit operations.

Initial estimation of the total number of trays of the main distillation column, placement of feed and side streams, and steam flow rate in the simulation environment are accomplished in the conceptual design environment.

In addition, convergence of the rigorous model is enhanced by using initial estimates of internal profiles generated at the conceptual design level despite of the highly non-ideal behavior of the multicomponent azeotropic mixture. Applying the same philosophy to estimate initial values for design and operating variables of the whole process, optimal values for a cost-effective bio-ethanol purification plant are reported.

The methodology is applied to the purification process for a feed leaving the fermentation step of a conventional corn dry-grind processing facility producing 24 million liters/year of ethanol and 19 million kg/year distiller´s dry grains with solubles (DDGS). 22170 kg/hr of a mixture mainly composed by ethanol (10.80 % w/w) and water (88.98 % w/w) with traces of methanol (0.0226 % w/w) and fusel (0.2009 % w/w) are fed to the purification plant. A simplified flow diagram is shown in Figure 1.

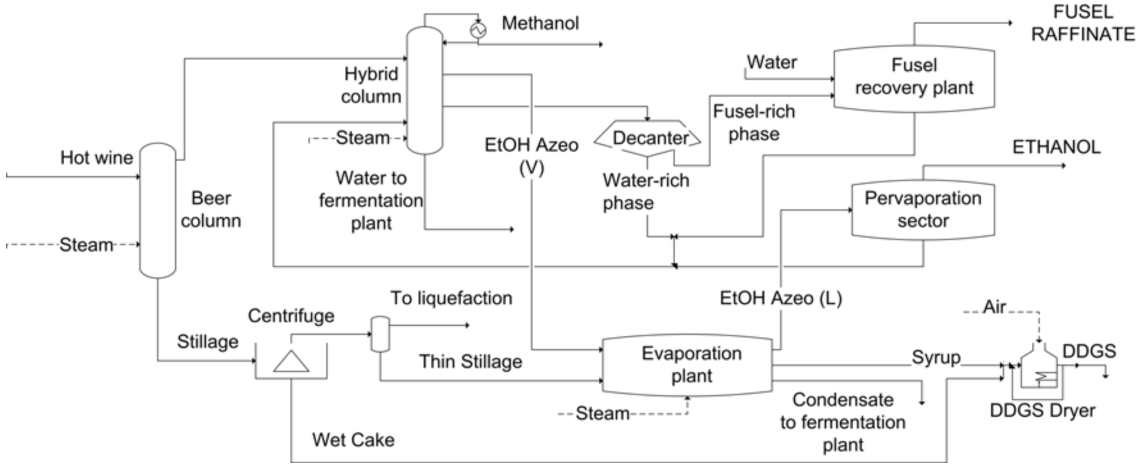

Figure 1. Simplified flow diagram of a bioethanol purification plant.

2. Initial Design

2.1. Beer Column

The ethanol and components in traces produced during the fermentation step are captured almost totally by the vapor stream leaving the stripping column. The minimum energy demand of the process (calculated as the minimum reboil ratio) is obtained using the lever arm rule by setting the bottom product as high purity water and the composition of the vapor in equilibrium with hot wine. In other words, a pinch at the top of the stripping column is considered. Figure 2 schematically shows how products of a column with an infinite number of stages move along the mass balance line as the actual reboil ratio takes values above or below the "minimum".

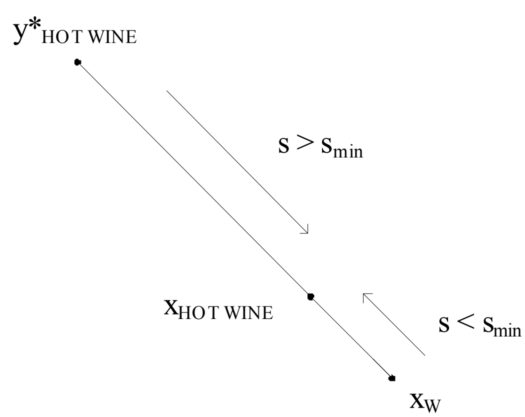

Figure 2. Influence of actual reboil ratio on the products of a column with an infinite number of separation stages.

The following steps are performed to obtain a quasi-optimal feasible design:

i) determine the maximum feasible separation and minimum energy demand (s_{min}) by applying pinch theory. An equilibrium calculation that can be performed in a conceptual model framework like DISTIL (Hyprotech, 1999) is required for such task;

ii) calculate the reboil ratio s as 1.05 s_{min};

iii) set a value for the number of stages N;

iv) simulate a stripping column with reboiler and once converged, replace the reboiler with live steam considering the reboiler duty and the latent heat of condensation of steam. This task can be done in a simulation framework like Hysys (Hyprotech, 1999).

A feasible column design was obtained, with 38 equilibrium stages, a column diameter of 0.9 m, a section pressure drop of 34.7 kPa and a steam flow rate of 3600 kg/h. The values obtained for the number of equilibrium stages and steam demand, together with the composition of ethanol in the outlet stream (51.52 % w/w) agree well with results presented in Kwiatkowski et al. (2006). Table 1 shows the "limiting" compositions of the streams entering and leaving the stripping column together with the minimum value of the reboil ratio s_{min}.

Table 1. Overall mass balance and energy demand of a beer column with and infinite number of stages (DISTIL).

	$x_{Hot\ wine}$	$y^*_{Hot\ wine}$	x_W	s_{min}
Methanol	0.000137	0.000659	0	
Ethanol	0.045288	0.303358	0	$= (x_W - x_{Hot\ wine})/(x_{Hot\ wine} - y^*_{Hot\ wine})$
Water	0.954135	0.692560	1	= 0.1753
1-Pentanol	0.000440	0.003423	0	

2.2. Hybrid Column

A conceptual design and rigorous simulation process is proposed for the separation of a multicomponent mixture, formed by ethanol and water with traces of methanol and fusel, in a single column. First, ethanol and methanol are lumped into one pseudo-component in order to obtain a first estimation of steam flow rate, number of stages necessary to separate an ethanol-rich stream from a fusel-rich stream, feed stage and side stream location (DISTIL). Rigorous simulation of the quaternary mixture is performed in the Hysys environment, where separation between a methanol-rich stream and an ethanol-rich stream is considered by taking into account the distillation line departing from the composition of the distillate (performed in the conceptual environment DISTIL). Finally, both columns are integrated into a single one (Hysys).

2.2.1. Side-Stream Column

For obtaining a feasible design, three steps were performed:

i) calculate $s_{min}^{(t)}$ for the separation ethanol/water/1-pentanol (DISTIL),

ii) estimate the number of equilibrium stages $N_{stages}^{(t)}$, feed stage $N_{feed}^{(t)}$ and side stream location $N_{Side\ Stream}^{(t)}$ for $s^{(t)} > s_{min}^{(t)}$ (DISTIL),

iii) simulate the quaternary system (Hysys) for the design and operating variables obtained in step ii), iv) calculate the steam flow rate $V_{steam}^{(q)}$ through the energy balance and simulate the column without reboiler (Hysys), v) simulate the system side-stream column plus decanter and water-rich phase recycle (Hysys).

Table 2 presents the results of the conceptual design performed in DISTIL[6], steps i) and ii), for the ternary mixture ethanol/water/1-pentanol, the latter used to approximate the behavior of the component fusel.

Table 2. Results for the ternary system ethanol/water/1-pentanol (DISTIL).

$R_{min}^{(t)}$ / $S_{min}^{(t)}$	2.839 / $\underline{1.00}$
$R^{(t)}$ / $S^{(t)}$	2.839 / $\underline{1.00}$
$N_{stages}^{(t)}$ [including condenser and reboiler]	17 [0 + 1-15 + 16]
$N_{feed}^{(t)}$/ $N_{Side\ Stream}^{(t)}$	4/11

Compositions of both ethanol and fusel in the bottom stream were selected taking into account the behavior of the residue curve (DISTIL) corresponding to the liquid in equilibrium with the vapor feed in the neighborhood of water vertex. As both for the ternary and quaternary mixture, the residue curve approaches the water vertex with compositions of ethanol above the mole fraction of fusel, the selected bottom composition reflects this behavior. The side stream is located inside the liquid-liquid gap as this stream will be separated in a decanter into a fusel-rich phase (feed to the fusel plant) and a water-rich phase (recycle to column).

Minimum reboil ratio for the given separation does not require an infinite number of stages. This behavior can be explained in terms of bifurcation of adiabatic profiles and it will be subject of further analysis in future work.

2.2.2. Methanol Column and Hybrid Column

The distillate stream of the side-stream column contains small amounts of methanol that must be separated from ethanol to agree with stringent quality standards (0.1 % V/V methanol in dehydrated ethanol at 20 ^{o}C). At a first glance, this separation could be performed in another distillation column. A different alternative would be to integrate this column with the side-stream column. The distillate line (DISTIL) corresponding to the distillate composition of the side-stream column resembles the behavior of the internal profile at total reflux and it can be considered as a good approximation to the actual operation of the methanol rectifying column, as the distillate flow rate of this column is low enough to produce a high reflux ratio. Therefore, it is possible to estimate the optimal number of stages in the rectifying section of the hybrid column as the number of trays necessary to separate the methanol in excess from the ethanol-rich stream. The methanol-rich distillate stream will also contain small amounts of ethanol and water due to the distillation line running from pure methanol to ethanol-water azeotrope.

A loss of about 0.18 % w/w of ethanol in methanol-rich distillate occurs. The side streams are located near the maximum in ethanol (ethanol-rich stream, 88.98 % w/w) and fusel (fusel-rich stream, 18.5 % w/w), respectively. The column has 35 equilibrium stages, a column diameter of 1.372 m, a section pressure drop of 11.8 kPa and a steam flow rate of 1800 kg/h. The vapor ethanol-rich stream is diverted to the first effect of the evaporation sector to provide heating while minimizing the steam demand of the plant. The condensed ethanol-rich stream is then fed to the pervaporation sector to remove the excess water.

2.2.3. Fusel Plant and Pervaporation Sector

The fusel-rich stream leaving the decanter is fed to the fusel sector where the stream is washed with water to recover about 96 % of the incoming ethanol. The resulting water-rich stream is recycled to the hybrid column. An overall amount of 363 kg/h wash-water and seven separation steps are necessary for this task. The conceptual design of a cross-flow operation is performed using DISTIL, while process simulation is done in Hysys.

A conceptual design of pervaporation (PVA/PAN MOL 1140 membrane by GFT, Germany) following the model proposed by Vier (1995) and Bausa and Marquardt (2000) was implemented in Delphi environment (Borland, 1997) to determine pseudo optimal operating values for both maximum temperature (90 ^{o}C) and permeate pressure (2.026 kPa). The model was also implemented in Hysys as a user operation extension, which calculates the required membrane area a_{req} as $a_{req} = 1.25\ a_{min}$ (Bausa and Marquardt, 2000). Both heat and refrigeration duties are calculated in Hysys from the energy balance. Behavior of trace components is taken into account by using water-alcohol separation factors. Approximate values were taken from D. Van Baelen et al. (2005). High purity bioethanol (99.5 % v/v) is obtained with an actual membrane area of 930 m^2, while the water-rich permeate is recycled to the hybrid column.

2.2.4. DDGS Plant

The co-product plant is formed by a decanter centrifuge which separates the bottom stillage from the beer column in a wet cake (35 % solids, 2683 kg/h water) and a thin stillage (18443 kg water/h). Approximately 4626 kg water/h is recycled into the second step of the liquefaction process, while 13817 kg water/h is feed to a three-effect evaporator. The resulting syrup (35 % solids, 1287 kg water/h) is mixed with the wet cake coming from the centrifuge and sent to a rotary drum dryer. While the multiple effect evaporator is simulated in Hysys, only mass and energy balances for the dryer are incorporated in Hysys. The conceptual design of the dryer is performed according to the method presented in Ulrich and Vasudevan (2004) and data from National Corn-To Ethanol Research Center (2005-2007). Table 3 summarizes the investment and operation costs of the DDGS sector. The operation cost of 35.9 \$/ton DDGS agrees well with the value reported by Batelle Memorial Institute (2005).

Table 3. Operation (\$/ton DDGS) and Investment (\$) Costs corresponding to DDGS plant.

Item	Characteristics	Invest./Op. Cost*	Invest./Op. Cost †
Rotary Dryer	D [m]= 1.664 L [m]= 13.31 τ [min]= 19.6 rpm= 2.869 Q_{air} [kg/h]= 39150 $\eta_{Nat.\ Gas}$ = 0.048‡	$1.39\ 10^6$/19.74	$1.57\ 10^6$
Evaporator	$Area_{overall}[m^2]$= 940 Pressure[kPa]= from 10-30 kPa Q_{steam} [kg/h]= 2700	$1.523\ 10^6$/16.16	$1.47\ 10^6$
Decanter Centrifuge		$1.07\ 10^6$§/not calculated	$1.07\ 10^6$

3. Evolutionary Optimization

Once an initial design is obtained, the following improvement opportunities were tested: i) design of the beer column in the neighborhood of minimum energy demand (done from the very beginning of design process), ii) heat integration between the hybrid column and evaporation first effect (1270 kg/h of steam are saved), iii) heat recovery from the hot air leaving the dryer (saving 0.014 kg natural gas/kg water evaporated).

Finally, a change in distillate composition of the hybrid column is proposed in order to capture the trade-offs between distillation and pervaporation costs. Resorting again to the conceptual design of the hybrid column for a set of distillate compositions, results shown in Figure 3 are obtained. The decrease of investment costs for distillate compositions richer in ethanol is related to a decrease in the membrane area needed to obtain dehydrated bioethanol (a_{req}=848 m^2). Table 3 shows both investment and operating costs of the quasi-optimal plant. All cases include improvements i), ii) and iii) mentioned above. Investment

* From Ulrich & Vasudevan (2004)
† Overall operating costs = 34.55 \$/ton DDGS.
‡ kg natural gas/ kg of water evaporated.
§ From Batelle Memorial Institute (2005)

and operation costs are reduced by 6.64 % with respect to the base case and by 11.48 % with respect to the worst case analyzed. Cost coefficients used to obtain the reported values are C_{steam}=2.396E-2, C_{water}=5.73E-3, C_{refr}=3.824E-2, C_{electr}=0.08 all in [$/kWh], $C_{nat\ gas}$=289 $/tn, $C_{memb\ repl}$ = 400 $/m^2.

Table 4. Overall costs for a bioethanol plant producing 24 million liters/year. The facility considers both the ethanol and co-product processing plants.

	Investment, $	Operating $/h	Investment, $/h	Total, $/h
DDGS Plant	3.985 E+06	96.37	81.07	177.44
Separation	3.768 E+06	117.96	76.66	194.62
Total	7.753 E+06	214.33	157.73	372.06

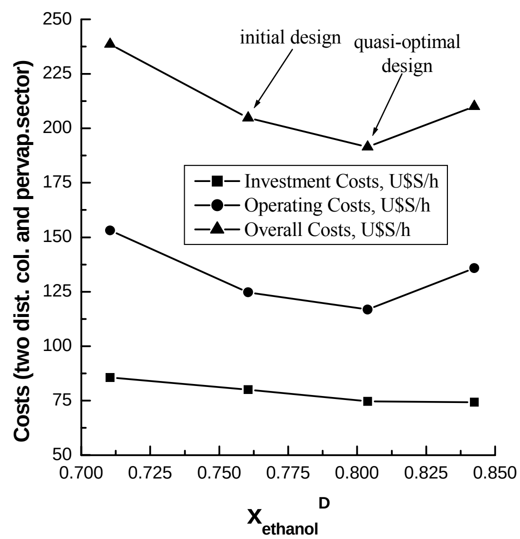

Figure 3. Overall investment and operating costs for the two distillation columns and pervaporation sector versus ethanol mole fraction in the distillate of the hybrid column.

4. Conclusions

A cost effective design for a bio-ethanol separation plant using conceptual design followed by rigorous simulation is found. The advantage of the method is that the systematic use of conceptual models allows the designer to capture the main characteristics of each operation involved in the process.

The minimum in the operation costs corresponds to a minimum in the steam flow rate of the hybrid column (1600 kg/h). The minimum in steam flow rate can be only explained by the presence of the fusel component, which influences both the energy demand and feasible products of the process. Therefore, designs based on the binary system ethanol-water do not represent the system behavior in an accurate way. From this consideration emerges the importance of properly determining the amount of trace components that enter the purification process.

Some other membranes should be considered as alternatives for the pervaporation sector in order to improve fluxes and selectivities, as it was shown that the hybrid process is economically attractive enough to promote future research efforts.

5. Acknowledgements

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References

Batelle Memorial Institute, Pacific Northwest Division, 2005, Quantifying Biomass Resources for Hydrothermal Processing II.

Bausa, J. and W. Marquardt, 2000, Shortcut Design Methods for Hybrid Membrane/Distillation Processes for the Separation of Nonideal Multicomponent Mixtures, Ind. Eng. Chem. Res., 39, 1658-1672.

Borland International Inc., 1997, Scotts Valley, USA, Delphi 3 User Manual.

Hyprotech Ltd., 1999, Calgary, Canada, Hysys & Distil User Manuals.

Kwiatowski, J. R; McAloon, A. J.; Taylor, F. and D. B. Johnston, 2006, Modeling the Process and Costs of Fuel Ethanol Production by the Corn Dry-Grind Process, Industrial Crops and Products, 23, 288-296.

National Corn-To Ethanol Research Center, 2005-2007, Utilizing the National Corn-to-Ethanol Pilot Plant to Develop a Predictive Model for Distillers Dried Grain for the Fuel Ethanol and Animal Feed Industries.

Ulrich, G. D. and P. T. Vasudevan, 2004, Chemical Engineering Process Design and Economics, A practical guide. 2nd ed., Process Publishing, Durham, New Hampshire.

Van Baelen, D.; Van der Bruggen, B.; Van den Dungen, K.; Degreve, J. and C. Vandecasteele, 2005, Pervaporation of water-alcohol mixtures and acetic acid-water mixtures. Chemical Engineering Science, 60, 1583-1590.

Vier, J.,1995, Pervaporation azeotroper wässriger und rein organischer Stoffgemische-Verfahrensentwicklung und –integration, Ph. D. Thesis, Institut für Verfahrenstechnik, RWTH Aachen, Shaker Verlag, Aachen, Germany.