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MULTIVARIATE STATISTICAL OPTIMIZATION OF THE ETHANOL FUEL DEHYDRATION PROCESS USING IONIC LIQUIDS

Article Highlights
- The desirability function assesses simultaneously several variables and their effects on responses
- Ionic liquids are promising solvents for the ethanol dehydration process
- Significant improvements in the processes with only minor modifications of a preexisting design

Abstract

In this work, the ethanol fuel dehydration process was optimized using the Aspen Plus® simulator and a multivariate statistical technique based on the desirability function. The suitability of the ionic liquids 1-methylimidazolium chloride ([Mim][Cl]), 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]), as extractive distillation entrainers, was also evaluated and compared to the conventional solvents, ethylene glycol and cyclohexane. Among the solvents studied, [Mim][Cl] required the lowest energy consumption, about 8% less energy use when compared to the optimized process using ethylene glycol. The multivariate statistical techniques employed were effective in the optimization of the extractive distillation processes as the process energy consumption could be minimized while achieving ethanol purity in agreement with the current specifications as well as obtaining a high solvent recovery. With the desirability approach it was possible to improve the process performance with little or no modification of existing processing plants.

Keywords: bioethanol, desirability, energy, extractive distillation, ionic liquid, optimization.

The increasing contribution of liquid biofuels to the world energy matrix is a consequence of the growing concern about environmental issues and the adoption of public policies to reduce fossil fuel usage. One important liquid biofuel is ethanol. Ethanol can be used directly or as ethanol/gasoline blends in internal combustion engines with spark ignition. The former is hydrated ethanol fuel (HEF), containing about 5 vol.% water, while the latter is dehydrated ethanol fuel (DEF) with a water content of about 0.5 vol.% [1].

Brazil and the United States of America together account for 85% of the global ethanol fuel production [2], two largest producers of ethanol fuel in the world, with distillation still as the dominant ethanol recovery process [3,4,5]. Particularly in the northeast region of Brazil, the process of ethanol dehydration by azeotropic distillation continues to be the most used as the majority of industrial plants are very old. However, the adoption of the molecular sieve technology is growing, especially for new industrial units.

In those units where DEF is produced by azeotropic and extractive distillation, the solvents cyclohexane [6] and ethylene glycol (EG) [7-9] are widely used. As the use of cyclohexane presents environmental and exposure risks, new technologies to dehydrate ethanol are preferred, among which are the

use of molecular sieves, membranes and extractive distillation using less toxic and more efficient solvents such as EG and ionic liquids (ILs) [10]. ILs have the advantage of having a good ability for separation, easy handling and low contamination in distilled products [11,12]. Examples of the ILs used for dehydration of ethanol are: 1-butyl-3-methylimidazolium tetrafluoroborate and 1-ethyl-3-methylimidazolium tetrafluoroborate [13], 1-butyl-3-methylimidazolium chloride [14], 1-ethyl-3-ethylimidazolium diethyl phosphate [15] and 1-hexyl-3-methylimidazole chloride [16]. A modeling and simulation study on extractive distillation using ILs showed advantages with respect to the distillate purity and recovery [17]. Imidazolium-based ILs were compared and the process optimized using a univariate procedure of sensitivity analysis [18]. A high-purity (>99.9 mol%) ethanol was achieved with a lower energy consumption compared to conventional solvents.

Optimization through sensitivity analysis is a univariate procedure. Generally, this approach is not suitable for the evaluation of phenomena that depend on many variables as it cannot estimate the interdependency among the variables. By neglecting the interaction among variables, the resulting optimum does not necessarily correspond to the global optimum.

The optimization of a process can be accomplished, in general, by means of deterministic or stochastic approaches. In the first class of methods, all the steps can be predicted if the starting points are known. In other words, a deterministic method always leads to the same response if it starts from the same initial point. In contrast, stochastic methods have a random character. Several choices are made based on random numbers, drawn at runtime. Both approaches are widely used in optimization problems in chemical engineering when the goal is to maximize or minimize a given response while keeping others subjected to certain constraints [19,20].

The deterministic approach is composed of traditional optimization methods (direct and gradient-based methods) and has the disadvantages of requiring the first and/or second order derivatives of the objective function and/or constraints, and not being efficient in non-differentiable or discontinuous problems. In addition, the deterministic methods are dependent on the initial conditions chosen. The stochastic approach does not have these disadvantages, since it does not need to have any information about the search space, requiring only an objective/adequacy function that assigns a value to any solution [20]. However, even if starting from the same initial point, each run will follow its path, possibly leading to

a different final response. It is important to remark that global optimization can only be guaranteed with deterministic methods. This is not guaranteed beforehand with stochastic techniques due to their probabilistic character. Both approaches are used when optimizing many factors and responses simultaneously. The application of these optimization approaches to separation processes has been reported by several authors [21-27].

Another optimization strategy is the use of a multivariate statistical optimization methodology, which consists of experimental design strategies to explore efficiently the space of the process variables; and empirical statistical modeling to develop an approximate relationship among the response (dependent variables) and the process variables (independent variables) in order to find optimized conditions [28]. Using this approach, interpretation of the models' coefficients (or main and interaction effects) contributes to enhancing process understanding.

The use of multivariate statistical optimization techniques along with process simulation still has not gained widespread usage. The ethanol dehydration process simulation and the use of response surface methodology to evaluate the interaction of the variables and their effects on the process can be found in the literature [29-32]. Their objective was to maximize the distilled ethanol concentration and to minimize the energy consumption. For these purposes, different surfaces were evaluated separately in order to identify a condition that would simultaneously satisfy the responses studied. This strategy may be satisfactory when different responses show similar behavior upon changing factor levels. When the responses have a certain degree of divergence, however, it is difficult to find a combination of the factor levels that simultaneously satisfies all the responses under investigation. A change in the level of one factor may improve a specific response while it may have a deleterious effect on the other responses [33]. A better approach to deal with multiple responses is to use mathematical functions to combine different responses into one, such as the desirability function proposed by [34]. Derringer's desirability function has proved to be efficient in optimizing processes [35,36]. However, the usefulness of the desirability function together with process simulation has not yet been reported in the literature.

In this work, the ethanol dehydration process by extractive distillation was optimized using multivariate statistical techniques, which consisted of simultaneously evaluating the relationship among several process variables through experimental design and sta-

tistical empirical modelling. The goal was to improve the performance of the process by means of simple modifications in an existing industrial plant. The desirability function was used to identify the set of factors that simultaneously optimize multiple responses related to the purity of the produced ethanol fuel and energy consumption. Results were compared to azeotropic distillation using cyclohexane, this still being a common process in the sugarcane ethanol industry. The Aspen Plus® simulator was employed to carry out the simulations with conventional process plant configurations. The following ILs were used as extractive distillation entrainers: 1-methylimidazolium chloride ([Mim][Cl]), 1-ethyl-3-methylimidazolium chloride ([Emim][Cl]), 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-hexyl-3-methylimidazolium chloride ([Hmim][Cl]).

METHODOLOGY

Process simulation

Figure 1a shows the simulated process flowsheet of the extractive distillation process [17]. The process is composed of the extractive distillation column (C-Column), which is fed with HEF and the solvent. Its distillate is DEF and the bottom stream is a mixture of water and solvent (water + solvent) which

in turn is sent to the second column, the solvent recovery column (P-Column). The P-column separates the water (as the distillate), from the solvent, which is recovered at its base and recycled to C-column along with the pure solvent make up (MKUP stream).

The simulated azeotropic distillation process is shown in Figure 1b [6,37]. Cyclohexane was used as the separation agent. The process consists of two distillation columns: the first column (C-Column) is the azeotropic column where ethanol is rectified from the HEF feed, reflux and recycle streams. The bottom product is the DEF. The distillate is an azeotropic mixture of solvent, ethanol and water, separated into organic and aqueous phases in a decanter. The majority of the solvent is recovered in the organic phase which returns to the C-column as a reflux stream along with the pure solvent make up (MKUP feed). The aqueous phase is fed to the P-column for solvent recovery; its bottom product is recovered water and the distillate is a mixture rich in ethanol and cyclohexane which is then recycled to the C-column. The column model used for the simulations was the rigorous RadFrac module available in Aspen Plus®.

Thermodynamic model

A simplified vapor-liquid equilibrium (VLE) relation for the ethanol/water/solvent ternary mixture was used because of the low pressures involved:
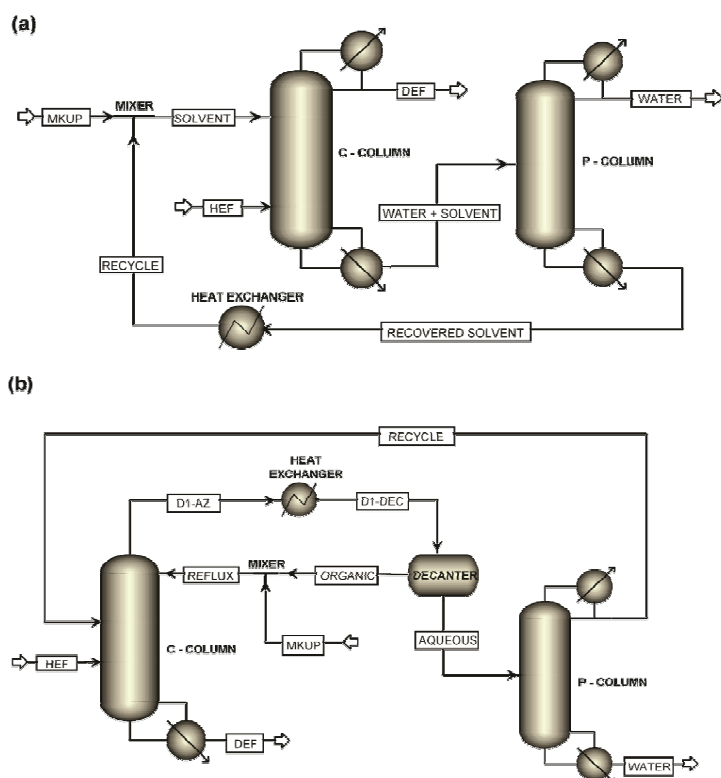

Figure 1. Process flowsheet of the extractive (a) and azeotropic (b) distillation processes.

$$Py_i = x_i \gamma_i P_i^{vap} \tag{1}$$

where P is the total pressure, y_i is the vapor phase mole fraction of component i, x_i is the liquid phase mole fraction of component i, γ_i is the activity coefficient of component i, and P_i^{vap} is the pure component i vapor pressure. Activity coefficients were calculated using the NRTL model [38]. Despite the fact that this model was developed for systems involving non-electrolytes [39], it has been widely used for mixtures with ILs [14,18,40,41].

The pure component properties were used as given in the Aspen Plus® databank, except for the ILs, not found in the database. In this case, the ILs were inserted into the simulator as pseudo-components. In order to estimate their vapor pressure, the data shown in Table 1 are introduced along with their pseudo-component definition.

The NRTL binary interaction parameters available in the Aspen Plus®.databases were used for the well-known ethanol/water/cyclohexane and ethanol//water/ethylene glycol ternary mixtures. For the systems with ILs, the NRTL binary interaction parameters were used as presented by [47] ([Mim][Cl]), [40] ([Emim][Cl]), [14] ([Bmim][Cl]) and [16] ([Hmim][Cl]).

Simulation setup

Table 2 presents the operational conditions for the simulated azeotropic [37] and extractive [17] distillation processes. In all cases, a flow rate of 100 kmol/h with a mass fraction of 95.2% ethanol was adopted for the HEF feed stream. A mass fraction greater than 99.3% ethanol was also specified for the DEF stream. Pressure in all distillation columns was set at 101.3 kPa [18,30,31].

Experimental design

Simultaneous evaluation of process factors was carried out using the Statistica® software, version 8. The factors evaluated were: reflux ratio of the dehydration (C-column) and recovery (P-column) columns, solvent to feed ratio (*S/F*), HEF feed stage, solvent feed stage and the recovery column (P-column) feed stage. The evaluated responses were: DEF purity (% mass), solvent recovery (%), purity of recovered solvent (% mass) and energy consumption per unit mass of DEF produced.

Initially, a screening of the six factors studied was performed through an experimental design, in order to choose the most significant factors. Then, using these most-significant variables, central composite designs were used to find the optimized condition. In the screening step, a six-factor full factorial design (with a central point) was used for each solvent, except for the azeotropic distillation process using cyclohexane in which only five factors could be studied. This is justified by the fact that the reflux ratio of the C-column is determined by the liquid-liquid phase splitting in the decanter. The C-column condenser was represented by a combination of a heat exchanger and a decanter (Figure 1b). Table 3 presents the levels of the factors studied, which were defined based on a previous sensitivity analysis.

Normal probability plots were employed in order to identify the significant factors for the process, as it is not possible, in simulations, to estimate the experimental random error. After selecting the most significant factors, factor levels were expanded using central composite designs (CCD), and the desirability function was used to find the optimal conditions.

Table 1. IL basic properties used in the creation of the pseudo-components in the simulator; NBP - normal boiling point

IL	Molecular formula	Molar mass (g/mol)	Density (kg/m^3)	*NBP* / K	Reference
[Mim][Cl]	$C_4H_7ClN_2$	118.56	1183.0	504.8	[42,43]
[Emim][Cl]	$C_6H_{11}ClN_2$	146.62	1186.0	484.6	[44]
[Bmim][Cl]	$C_8H_{15}ClN_2$	174.67	1080.0	547.5	[45]
[Hmim][Cl]	$C_{10}H_{19}ClN_2$	202.73	1040.4	593.2	[46]

Table 2. Process data used in the simulations

Specification	[Mim][Cl]	[Emim][Cl]	[Bmim][Cl]	[Hmim][Cl]	EG	Cyclohexane
Number of stages of C-column	33	33	33	33	33	31
HEF feed stage	20	20	20	20	20	15
Solvent feed stage	6	6	6	6	4	10
C-Column reflux ratio	2	2	2	2	1.4	-
Number of stages of P-column	12	12	12	12	12	22
Feed stage of P-column	11	9	9	11	4	11
P-Column reflux ratio	2	2	2	2	1.5	0.35

Table 3. Design factors and levels used in the screening step

Factor	[Mim][Cl]			[Emim][Cl]			[Bmim][Cl]			[Hmim][Cl]			EG			Cyclohexane		
	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+
(1) HEF feed stage	16	24	32	20	26	32	18	25	32	20	26	32	22	27	32	11	14	17
(2) Solvent feed stage	4	11	18	2	5	8	2	7	12	2	5	8	3	6	9	2	6	10
(3) Feed stage of P-column	3	7	11	3	6	9	3	6	9	2	6	10	2	5	7	2	11	20
(4) Reflux ratio of C-column	0.5	1.25	2.0	0.5	1.25	2.0	1.2	1.6	2.0	0.5	1.25	2.0	0.8	1.22	1.65	-	-	-
(5) Reflux ratio of P-column	0.9	1.45	2.0	0.9	1.45	2.0	0.9	1.45	2.0	0.5	1.25	2.0	0.5	1.0	1.5	0.1	0.45	0.8
(6) *S/F*	0.19	0.24	0.28	0.25	0.28	0.31	0.30	0.35	0.40	0.44	0.46	0.48	0.55	0.60	0.65	0.110	0.115	0.121

In this approach, the individual responses were converted into values between 0 and 1, called individual desirability (d_i), where 0 and 1 represent undesirable and desirable responses, respectively [48]. In cases of response maximization, d_i was calculated by:

$$d_i = \begin{cases} 0, & y < L \\ \left(\dfrac{y-L}{T-L}\right)^s, & L \le y \le T \\ 1, & y > T \end{cases} \quad (2)$$

where y is the response being monitored, L is the lowest acceptable response and T is the target response. In addition, it is possible to weigh the response through the exponent s. In the cases of minimization of the response, d_i was given by:

$$d_i = \begin{cases} 1, & y < T \\ \left(\dfrac{U-y}{U-T}\right)^t, & T \le y \le U \\ 0, & y > U \end{cases} \quad (3)$$

U is the highest acceptable response and t is the response weighing parameter. A third possibility can be evaluated when the target value (T) is between the lowest (L) and the highest (U) values [48].

All the individual desirabilities were then combined by means of a geometric mean to calculate the global desirability D, given by:

$$D = \left(\prod_{i=1}^{m} d_i\right)^{1/m} \quad (4)$$

where m is the number of individual desirabilities. After the set of conditions that maximize the global desirability has been determined, the individual behavior of each response should be examined to ascertain that they are all within acceptable regions and with all constraints satisfied, and then analyze the practical feasibility [49].

RESULTS AND DISCUSSION

Residual curve maps analysis

The separation ability of the ILs as extractive distillation entrainers was initially evaluated by means of residual curve maps, as shown in Figure 2a-d. For comparison purposes, residual curve maps are also shown for EG and cyclohexane in Figure 2e and f, respectively. As can be observed, the ILs under study presented the same behavior as EG. As there are no stationary points in Figure 2a-e, a ternary mixture separation by extractive distillation is feasible.

For the ethanol/water/cyclohexane ternary (Figure 2f), on the other hand, there are three stationary points: binary azeotropes ethanol/cyclohexane at 64.92 °C, water/cyclohexane at 69.49 °C and ethanol/water at 78.15 °C. The unstable node for the ternary mixture at 62.39 °C defines three regions where the fed compositions will result in pure ethanol (region 1), pure water (region 2) and pure cyclohexane (region 3).

Factorial design screening

The complete factorial design with six factors shown in Table 3 was carried out in a preliminary screening stage for all solvents, except for cyclohexane where only five factors were taken into consideration. In all cases, the factorial design was performed again taking into consideration only the statistically significant factors from the previous step. This procedure was repeated until all remaining factors were significant. Analysis of the normal probability plots led to the results summarized in Table 4.

For illustration purposes, the normal probability plots for [Bmim][Cl] are shown in Figure 3. As can be seen, main effects 1, 2 and 4 and interaction between factors 1 and 4 are the most significant for the DEF purity and the recovered solvent purity responses (Figure 3a and c). For the recovered solvent purity, factor 6 also appears to be significant. In the case of the recovered solvent response (Figure 2b), the main effects 3, 4 and 5 and the interactions 3*4 and 3*5 were significant. For the energy consumption res
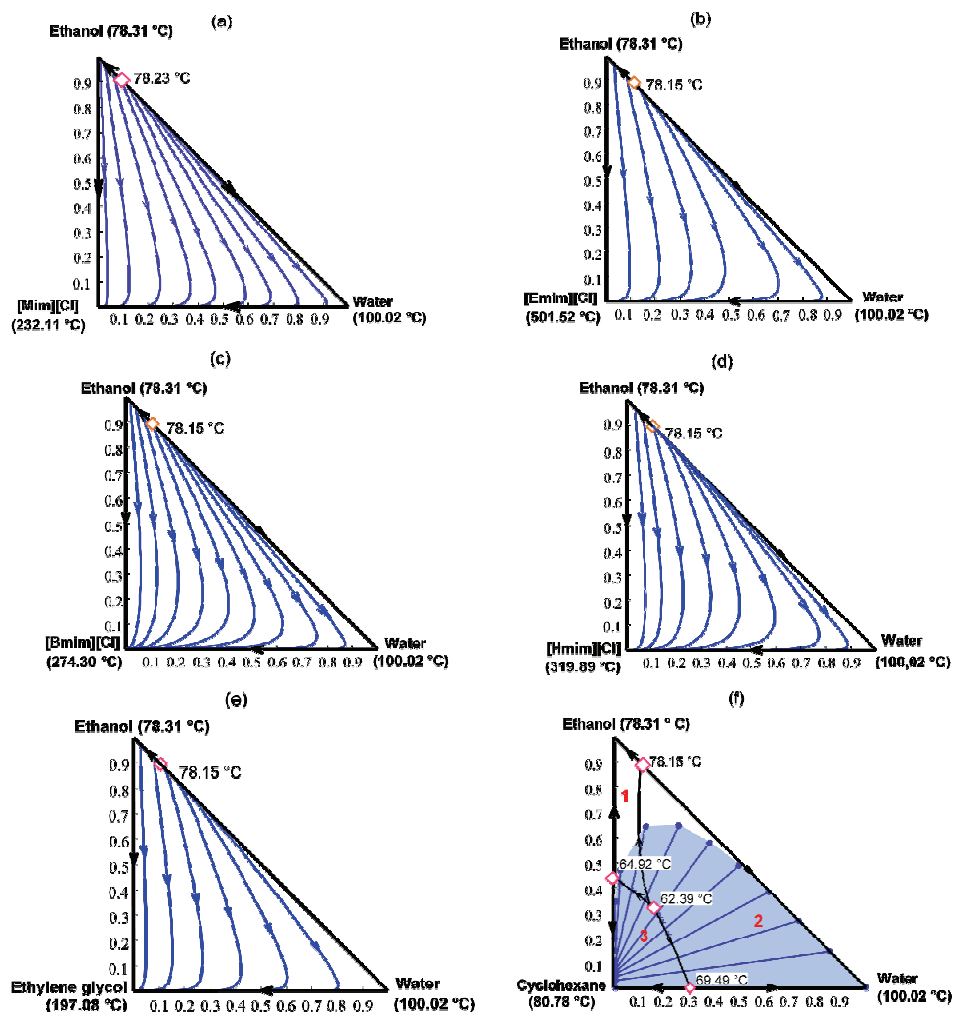
Figure 2. Residual curve maps for ethanol-water-solvent, where the solvent is: a) [Mim][Cl], b) [Emim][Cl], c) [Bmim][Cl], d) [Hmim][Cl], e) EG and f) cyclohexane.

Table 4. Factors and levels after the screening step

Factor	[Mim][Cl]			[Emim][Cl]			[Bmim][Cl]			[Hmim][Cl]			EG			Cyclohexane		
	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+	−	0	+
(1) HEF feed stage	-	-	-	20	26	32	-	-	-	-	-	-	-	-	-	-	-	-
(2) Solvent feed stage	-	-	-	-	-	-	2	7	12	2	5	8	-	-	-	2	6	10
(3) Feed stage of P-column	-	-	-	-	-	-	-	-	-	-	-	-	2	5	7	2	11	20
(4) Reflux ratio of C-column	0.5	1.25	2.0	0.5	1.25	2.0	1.2	1.6	2.0	0.5	1.25	2.0	0.80	1.22	1.65	-	-	-
(5) Reflux ratio of P-column	0.9	1.45	2.0	-	-	-	-	-	-	-	-	-	0.5	1.0	1.5	-	-	-
(6) *S/F*	0.19	0.24	0.28	0.25	0.28	0.31	0.30	0.35	0.40	0.44	0.46	0.48	-	-	-	0.110	0.115	0.121

ponse, the main effects of factors 4, 5, 6 and 2 are clearly significant.

Factor 3 seems not to be significant for any of the responses investigated. Factor 1 is only signific-ant for the following responses: purity of anhydrous ethanol and purity of recovered solvent, showing a negative signal for each. Thus, after observing the normal graphs and the responses for the design

matrix, factor 3 was the positive level and factor 1 at the negative level, as at these levels the best results show.

A new design was proposed for the remaining factors (factors 2, 4, 5 and 6). In this design, factor 5 only showed significance for the response of energy consumption, and by setting this factor at the negative level, lower values of energy were obtained. And
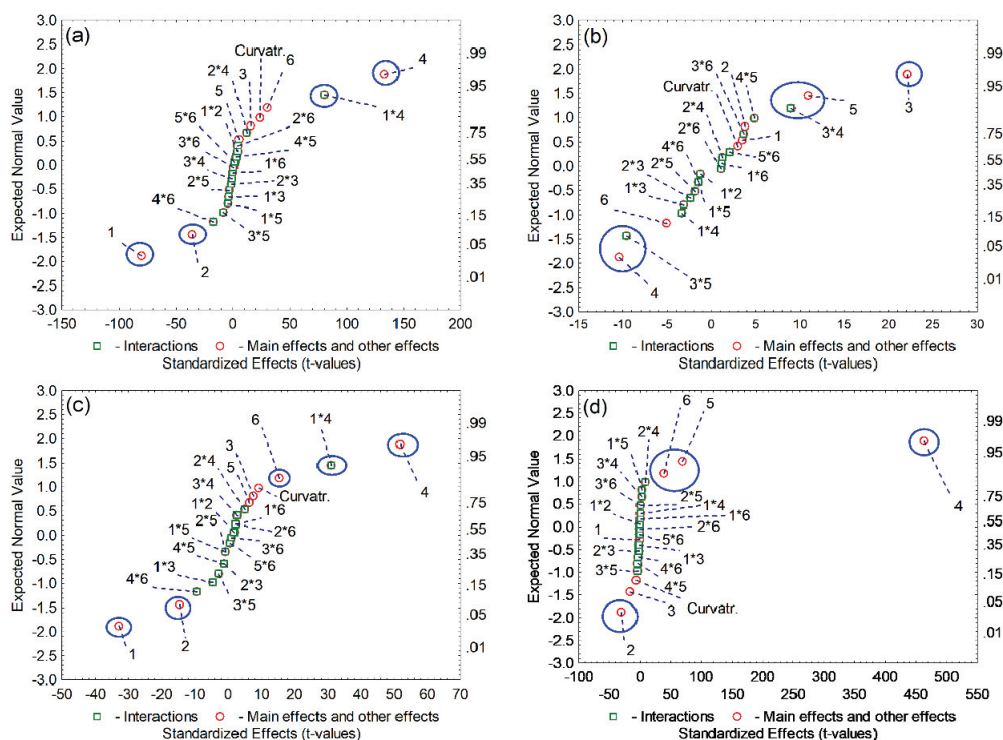
Figure 3. Normal probability plots for the 2^6 factorial design for the extractive distillation using [Hmim][Cl]; responses are: a) DEF purity, b) solvent recovery, c) purity of recovered solvent and d) energy consumption.

finally, a face-centered design of three factors (2, 4 and 6) was proposed.

In order to carry out the simulations, values for some factors, including the non-significant factors, were chosen as described next. [Mim][Cl]: non-significant factors 1 (HEF feed stage), 2 (solvent feed stage) and 3 (P-column feed stage) were all set at the negative level, 16, 4 and 3, respectively. [Emim][Cl]: non-significant factors 2 (solvent feed stage), 3 (P--column feed stage) and 5 (reflux ratio of P-column) were set at the positive (8), positive (9) and negative (0.5) levels, respectively. [Bmim][Cl]: non-significant factors 1 (HEF feed stage), 3 (P-column feed stage) and 5 (reflux ratio of P-column) were set at the positive (32), negative (3) and negative (0.9) levels, respectively. EG: non-significant factors 1 (HEF feed stage), 2 (solvent feed stage) and 6 (*S/F*) were set at the negative (22), negative (3) and positive (0.65) levels, respectively. Cyclohexane: non-significant factors 1 (HEF feed stage) and 5 (P-column reflux ratio) were set at 15 and 0.45, respectively.

Desirability function

Following the desirability definition, undesirable conditions (d_i = 0) were chosen as DEF purity less than 99.3% and purity of recovered solvent less than 99%. On the other hand, the desirable conditions (d_i = = 1) were defined as DEF purity greater than 99.7%

and purity of recovered solvent greater than 99.6%. Energy consumption and solvent recovery specifications were defined according to the results obtained for each experimental design. In the processes in which ionic liquids were used, it was not necessary to evaluate the response of the recovered solvent, since the recovery was 100% for all cases. The desirability function was generated in the Statistica® software. For illustration purposes, results for the extractive distillation process using the [Mim][Cl] IL are shown in Figure 4.

The curves in Figure 4 show the effect of each factor on the responses while the levels of the remaining factors are held at the specified values. The last column of graphs in Figure 4 shows the desirability previously set for each response. Taking factor 4 (C-Column reflux ratio) as an example, its effects on the responses can be observed in the first column on the graphs, where the first graph corresponds to the DEF purity. Its optimal point is located at level -1 of the design. A similar behavior was observed for the purity of the recovered solvent. At level -1, the energy consumption was minimized. Thus, level -1 meets the best combination of optimal conditions for factor 4, which is endorsed by the global desirability shown at the bottom left in Figure 4.

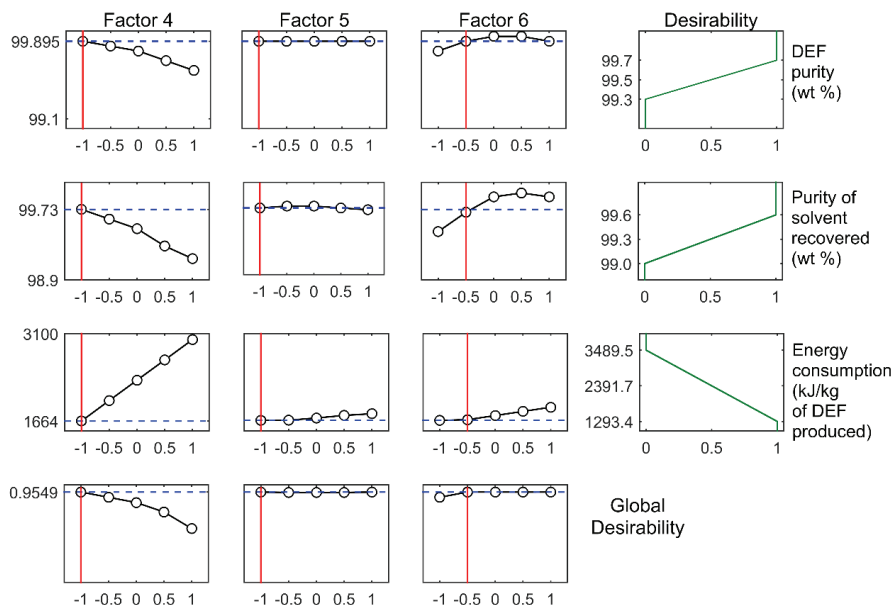The second column of graphs in Figure 4 shows the effects of factor 5 (P-Column reflux ratio). As can

Figure 4. Desirability function results for the extractive distillation process using [Mim][Cl] IL.

be observed, the response variation is smaller in comparison to factor 4, but DEF purity, purity of the recovered solvent and energy consumption also reach optimal conditions at level −1. As a result, the global desirability indicates that factor 5 meets all specifications at level −1.

Finally, the third column of graphs in Figure 4 presents the effects of factor 6 (S/F ratio). Here, the optimal conditions are observed at level -0.5 for DEF

purity, purity of the recovered solvent and energy consumption. Thus, the best condition for all the responses is located at level -0.5 as given by the global desirability.

The analysis described above was repeated for each process. Results are summarized in Figure 5. The decoded optimal levels are presented in Table 5 along with the responses obtained from process simulations at the corresponding levels. Table 5 also
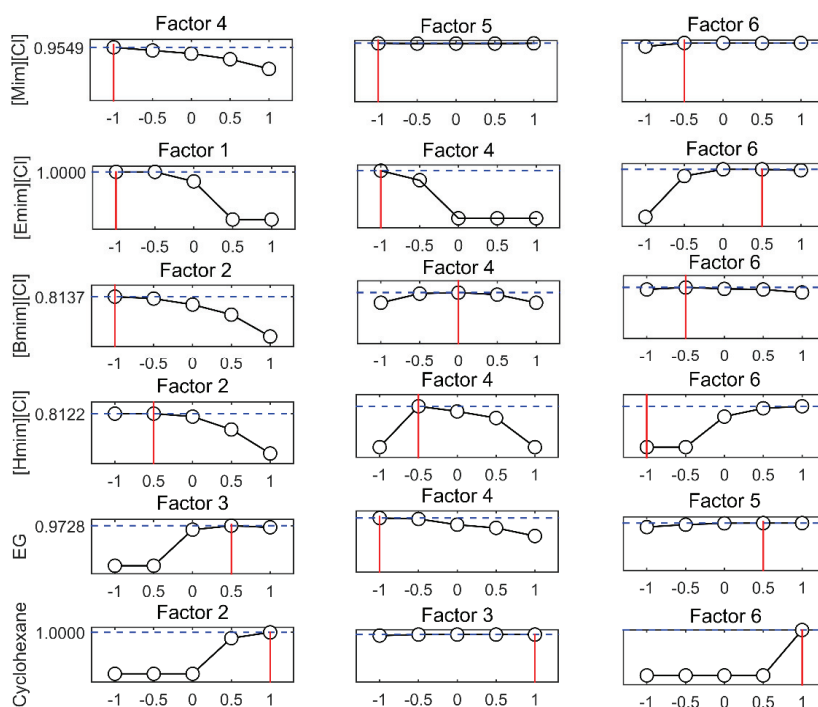

Figure 5. Global desirability for each simulated process.

Table 5. Comparison of simulation results for starting (S) and optimized (O) process conditions

Factor	[Mim][Cl]		[Emim][Cl]		[Bmim][Cl]		[Hmim][Cl]		EG		Cyclohexane	
	S	O	S	O	S	O	S	O	S	O	S	O
(1) HEF feed stage	20	16	20	20	20	32	20	20	20	22	15	15
(2) Solvent feed stage	6	4	6	8	6	2	6	4	4	3	10	10
(3) P-Column feed stage	11	3	9	9	9	3	11	10	6	6	11	20
(4) C-Column reflux ratio	2	0.5	2	0.5	2	1.6	2	0.9	1.4	0.8	-	-
(5) P-Column reflux ratio	2	0.9	2	0.5	2	0.9	2	0.5	1.5	1.25	0.35	0.45
(6) *S/F* ratio	0.19	0.22	0.25	0.295	0.30	0.325	0.44	0.48	0.60	0.65	1.20	1.21
Response												
DEF purity (mass fraction, %)	99.6	99.9	99.4	99.9	99.4	99.6	99.3	99.6	99.9	99.6	99.9	99.9
Solvent recovery (%)	100	100	100	100	100	100	100	100	100	99.2	97.08	97.25
Purity of solvent recovered (mass fraction, %)	99.3	99.7	99.3	99.9	99.6	99.7	99.6	99.8	99.9	99.6	95.2	95.3
Energy consumption (kJ/kg of DEF produced)	3078	1665	3631	2495	3482	3065	4072	3045	2340	1818	3101	3248

presents factors and the corresponding responses from simulations based on the data used for the screening step (Table 3). Detailed information for each optimized flowsheet is available upon request to corresponding author as the supplementary material.

As can be observed in Table 5, a DEF mass fraction purity ≥99.3% was obtained in all cases as well as a high solvent recovery, thus, reducing the amount of solvent needed make up. With respect to energy consumption, a decrease was observed in all cases under the optimized conditions, reaching 45.9% for the [Mim][Cl] process, except for the azeotropic distillation using cyclohexane where an increase of 4.7% was obtained. This observation can be rationalized by the fact that the feasible operating conditions for the azeotropic distillation process are constrained to a narrow region (Figure 2f) so that the starting setup can be used as the optimal set of conditions. However, for the majority of cases, the multivariate statistical technique used was effective in producing the specified DEF accompanied by a decrease in the energy consumption and requiring only small modifications of an existing process plant.

The optimized results obtained were compared with the literature from an extensive review of recent advances in the development of bioethanol recovery and dehydration processes [50]. Fifty-four publications were identified on the topic. They were classified according to the concentration of ethanol used in the process feed. Sixteen papers reported a process feed close to the azeotrope point of the ethanol/water mixture (90-95%), which was the EHF concentration we used in this article. These works were also classified according to the type of technology used for dehydration, all of them used distillation.

Hence, an approximate comparison was made with the cases that used hydrated ethanol feeds close to the azeotrope point. Table 6 presents a comparison of the energy consumption and DEF purity obtained in our study in relation to the most relevant works in the literature as well as other information about these publications.

The azeotropic distillation process simulated in this work presented energy consumption 36.1% lower than that presented by [6]. In the case of extractive distillation with EG, the energy consumption obtained in this study was 3.3% higher than that reported by [7] who used the same solvent, the difference being due to different simulation configurations. The use of the EG/calcium chloride mixture [30] presented an energy consumption 27.6% lower than the extractive distillation process with EG. Relative to EG and tetraethylene glycol [10], higher values of energy consumption were observed. However, in these cases only the energy used by the dehydration column was reported, so that the energy used in the solvent recovery step was not taken into account. Finally, EG [51], EG/glycerol mixture [52] and glycerol [53] presented higher energy consumptions when compared to EG case studied in this work.

In the case of IL, in our work, especially for [Emim][Cl] and [Bmim][Cl], based on the [17], there was a reduction of 23.9% and 29.7% in relation to energy consumption, respectively. Unfortunately, the same was not observed for [Hmim][Cl], with only a small difference of 1.2% between the cases studied relative to the results from [17]. Other ILs found in the

Table 6. Comparison of the energy consumption, DEF purity and HEF feed results for ethanol dehydration

Solvent	HEF feed wt.%	DEF purity wt.%	Energy consumption (kJ/kg of anhydrous ethanol)	Remarks	Reference
[Mim][Cl]	95.2	99.9	1665	-	Authors
[Emim][Cl]	95.2	99.9	2495	-	
[Bmim][Cl]	95.2	99.6	3065	-	
[Hmim][Cl]	95.2	99.6	3045	-	
EG	95.2	99.6	1818	-	
Cyclohexane	95.2	99.9	3101	-	
[Emim][Cl]	89.0	99.5	3278	-	[17]
[Bmim][Cl]	90.0	99.6	4359		
[Hmim][Cl]	93.0	99.6	3008		
[Bmim][SO4]	93.0	99.6	4118		
[Bmim][BF4]	93.0	99.5	8689		
[Emim][BF4]	93.5	99.9	2270	-	[18]
Tetraethylene-glycol	93.5	99.6	4600*	*Energy consumption calculation based on the dehydration column only	[10]
EG	93.5	99.6	3600*		
EG	93.5	99.9	2200	New operating flowsheet was proposed including three columns: an extractive distillation column, solvent recovery column, and a concentrator.	[51]
EG	93.5	99.9	1760	Simulation based on laboratory experiments and a pilot plant.	[7]
EG + Calcium Chloride	94.9	99.9	1425	Vacuum distillation used on the solvent recovery column	[30]
60% EG + 40% Glycerol	94.9	99.9	2018	Vacuum distillation used on the solvent recovery column	[52]
Glycerol	93.5	99.5	1900	Vacuum distillation used on the solvent recovery column	[53]
Cyclohexane	90.0	99.9	7900-14000	Dividing-wall column used for heterogeneous azeotropic distillation	[54]
Cyclohexane	93.5	*	4853	*Anhydrous ethanol obtained within specification	[6]
Gasoline	93.5	*	3180		

literature are included on the table in order to compare with energy consumption, indicating that all IL proposed in this article showed lower energy consumption.

The lowest energy consumption among the ILs presented was observed for [Mim][Cl], about 8% lower than that obtained for the optimized process with EG. Among the IL, the following order of increasing energy was obtained: [Mim][Cl] (1665 kJ/kg DEF) < [Emim][Cl] (2495 kJ/kg DEF) < [Hmim][Cl] (3045 kJ/kg DEF) ≈ [Bmim][Cl] (3065 kJ/kg DEF). The difference between the energy consumption of the last two ionic liquids is less than 1%. Among the studied ILs, [Mim][Cl] was found to be the most promising solvent for the production of anhydrous ethanol with high purity at lower energy levels, having the lowest *S/F* (0.22) required to separate the ethanol--water mixture.

CONCLUSIONS

The suitability of the ILs used for ethanol dehydration was evaluated with optimized process conditions presenting improvements when compared to base cases, except for azeotropic distillation using cyclohexane. This process is still used in the Brazilian industry, although its operational conditions are constrained to quite narrow ranges. As a result, the proposed starting setup may be taken to seamlessly be included at the optimal point. For the extractive distillation processes, however, it was possible to find optimal conditions meeting the specified goals. Among the ILs used as entrainers in the extractive distillation, [Mim][Cl] presented the best results with 8% less energy use when compared to the optimized process using EG. The use of the multivariate statistical technique and the desirability function made it possible to evaluate simultaneously the relationships among several process variables and their effects on the spe-

cified responses. This approach was effective in finding the optimal process conditions, making significant improvements possible in the processes studied with only minor modifications of a preexisting process plant. The application of this methodology to the energy intensive ethanol dehydration process is an important contribution to the sustainability of the sugarcane industry by increasing ethanol fuel competitiveness against fossil fuels.

Acknowledgments

Abbreviations list

[Mim][Cl]	1-Methylimidazolium chloride
[Emim][Cl]	1-Ethyl-3-methylimidazolium chloride
[Bmim][Cl]	1-Butyl-3-methylimidazolium chloride
[Hmim][Cl]	1-Hexyl-3-methylimidazolium chloride
EG	Ethylene glycol
HEF	Hydrated ethanol fuel
DEF	Dehydrated ethanol fuel
IL	Ionic liquid
NRTL	Non-Random Two Liquid
S/F	Solvent-to-feed ratio
CCD	Central composite design

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NAUČNI RAD

MULTIVARIJABILNA STATISTIČKA OPTIMIZACIJA PROCESA DEHIDRATACIJE ETANOLA KORIŠĆENJEM JONSKIH TEČNOSTI

U ovom radu, optimizovan je postupak dehidratacije etanola pomoću simulatora Aspen Plus® i multivarijabilne statističke tehnike zasnovane na funkciji poželjnosti. Pogodnosti jonskih tečnosti 1-metilimidazolijum-hlorida ([Mim] [Cl]), 1-etil-3-metilimidazolijum-hlorida ([Emim] [Cl]), 1-butil-3-metilimidazolijum-hlorida ([Bmim] [Cl]) i 1-heksil-3-metilimidazolijum-hlorida ([Hmim] [Cl]), kao modifikatora ekstraktivne destilacije, su procenjene i upoređene sa konvencionalnim rastvaračima, etilen-glikolom i cikloheksanom. Među korišćenim rastvaračima, [Mim] [Cl] je zahtevao najmanju potrošnju energije, oko 8% manje u odnosu na etilen-glikol. Korišćene multivarijabilne statističke tehnike bile su efikasne u optimizaciji procesa ekstraktivne destilacije, jer se potrošnja energije u procesu može svesti na minimum, dok se postiže čistoća etanola u skladu sa važećim specifikacijama i visok povraćaj rastvarača. Ovim pristupom bilo je moguće poboljšati učinak procesa sa malo ili bez modifikacije postojećih procesnih postrojenja.

Ključne reči: bioetanol, poželjnost, energija, ekstraktivna destilacija, jonska tečnost, optimizacija.