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Improvements on anhydrous ethanol production by extractive distillation using ionic liquid as solvent

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Abstract

Biorefineries use a variety of separation methods in order to produce high value co-products from different feed streams. The ionic liquids (IL) represent new classes of non-volatile selective solvents with large solubility, low solution viscosities, low toxicity. In this work, a computational study on extractive distillation using ionic liquids aiming to improve the properties of separation and lower energy consumption compared to conventional extraction agents, showing significant potential for this application, was developed. The ternary vapor liquid equilibrium data were taken from literature and the process was modeled and simulated using Aspen Plus TM process simulation environment. Computed results showed that 1-Butyl-3-methylimidazolium methyl sulfate ([emim][mSO₄]) consumes lesser energy per kilogram of anhydrous ethanol, obtaining an ethanol purity of 0.995 (in mass) and an ethanol percentage recovery of 99.9 wt%.

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Keywords: Biofuels; ionic liquids; azeotrope; extractive distillation

1. Introduction

Currently, worldwide, due to technological advances in the production of ethanol, there is great potential to reduce energy consumption and to avoid separating agent loss in sugar and alcohol industries, as well as to the increased production of hyperazeotropic ethanol (ethanol above azeotropic point with

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water). In this context, one of the research aims is to establish an upgrade and efficient method of ethanol dehydration in order to introduce innovations related to solvents used in conventional processes such as ethylene glycol [1]. Thus, extractive distillation with different extractive agents needs to be studied for the separation of azeotropic ethanol-water mixture with minimum boiling point (351.25 K) and ethanol mass composition of 0.956 ethanol at 101.325 kPa.

In order to increase the economic efficiency of ethanol fuel compared to the production of other fuels, several optimization strategies have been proposed involving the purification of ethanol, especially related to concentration and dehydration [2], steps that involve a large amount of energy [3].

Bearing this in mind, in this work, it is proposed an alternative and efficient technology for the production of anhydrous ethanol, comprising an intensified process through the use of different mass separating agents, more specifically ionic liquids, in the extractive distillation process. Ionic liquids (IL) are generally defined as organic salts, liquid below 373K and represent a new class of solvents, non-volatile and soluble. They have the advantages of high separation ability, easy operation and zero contamination of the distilled products, and are relatively new, with attractive features for applications in industrial processes, among them, employment as an agent of mass separation azeotropic mixtures or mixtures with close boiling points [4, 5]. Different IL's can replace toxic and hazardous components such as ethylene glycol, diethyl ether, pentane or benzene.

Several authors have studied phase equilibrium of mixtures ethanol/water/IL, showing that it is thermodynamically possible to obtain anhydrous ethanol using IL [6-15]. The authors and their respective IL's studies are reported in Table 1.

The literature present computational studies about azeotropic separation process for ethanol/water mixtures using [emim][BF₄] and [emim][DEP] with ethanol mass purity upper 0.995 [5, 11].

In this work, based on the fact that the dehydration of ethanol using IL is thermodynamically possible, the simulated process allows to confirm the possibility of applying the extractive distillation using IL, in order to get the separation of an azeotropic mixture and to check the features of ionic liquids as separating agents, comparing the efficiency of the process and evaluating different IL's in relation to other solvents.

The objective of this study was to model the ionic liquids and to simulate a system of two distillation columns (purification of ethanol and recovery of IL), using IL's as solvents to perform the separation of ethanol from the azeotropic mixture formed with water. Eight (08) IL's from Table 1 were analyzed in this study: [bmim][Cl], [emim][Cl], [bmim][mSO₄], [emim][BF₄], [bmim][OAc], [bmim][BF₄], [bmim][N(CN)₂] and [hmim][Cl]. These IL's were selected with the criteria of availability of physicochemical properties and equilibrium data published in the open literature [8, 9, 14].

Table 1. Application of ionic liquids as mass separating agents in the dehydration of ethanol. The respective experimental data for vapor liquid equilibrium are reported in the literature

| Ionic liquids | | Abbreviation | Reference |
|------------------------------|------------------------|-----------------------------|-----------|
| Cation | Anion | | |
| 1-Butyl-3-Methylimidazolium | Tetrafluoroborate | [bmim][BF ₄] | [11] |
| 1-Ethyl-3-Methylimidazolium | | [emim][BF ₄] | |
| 1-Butyl-3-Methylimidazolium | Chloride | [bmim][Cl] | [6] |
| 1-Methyl-3-Methylimidazolium | Dimethyl phosphate | [mmim][DMP] | |
| 1-Ethyl-3-Methylimidazolium | Diethyl phosphate | [emim][DEP] | |
| 1-Butyl-3-Methylimidazolium | Bromide | [bmim][Br] | [15] |
| | Chloride | [bmim][Cl] | |
| | Hexafluoride phosphate | [bmim][PF ₆] | |
| 1-Ethyl-3-Ethylimidazolium | Diethyl phosphate | [eeim][DEP] | [10] |
| 1-Ethyl-3-Methylimidazolium | Diethyl phosphate | [emim][DMP] | [12] |
| | Ethyl sulfate | [emim][ES] | [13] |
| 1-Hexyl-3-Methylimidazolium | Chloride | [hmim][Cl] | [7] |
| 1-Butyl-3-Methylimidazolium | Tetrafluoroborate | [bmim][BF ₄] | |
| 1-Ethyl-3-Methylimidazolium | | [emim][BF ₄] | |
| 1-Butyl-3-Methylimidazolium | Dicyanamide | [bmim][N(CN) ₂] | [9] |
| 1-Ethyl-3-Methylimidazolium | | [emim][N(CN) ₂] | |
| 1-Butyl-3-Methylimidazolium | Acetate | [bmim][OAc] | |
| 1-Ethyl-3-Methylimidazolium | | [emim][OAc] | |
| 1-Butyl-3-Methylimidazolium | Chloride | [bmim][Cl] | |
| 1-Ethyl-3-Methylimidazolium | | [emim][Cl] | |
| 1-Hexyl-3-Methylimidazolium | | [hmim][Cl] | |
| 1-Butyl-3-Methylimidazolium | Methyl sulfate | [bmim][mSO ₄] | [8] |

2. Methodology

The flowsheet of the extractive distillation process for modeling and simulation is presented in Figure 1. This flowsheet consists of a mixer (B1), two distillation columns (B2 and B3), a splitter (B4) and a heat exchanger (B5).

2.1. Description of Equipment Used in the Extractive Distillation Process

- Mixer (B1) mixes IL recycle with IL makeover.
- Ethanol purification column (B2) raising the ethanol concentration above azeotropic point. The products were water (at the bottom of the column) and ethanol (at the top of the column).
- IL Recovery column (B3) retrieves the IL used. The IL leaves at the bottom and the water leaves at the top.
- Splitter (B4) purges the system, preventing the IL accumulation.
- Heat exchanger (B5) cools the IL recycle and prevents a drop in the thermal efficiency in column B2.

2.2. Thermodynamics Modeling

The IL's were modeled as pseudocomponent in the Aspen Plus™ process simulation environment based on the molecular structure, using properties such as, molar mass, density of the liquid (ρ), heat capacity (C_p), normal boiling temperature (T_b), critical properties, and vapor pressure (P_v). The physicochemical properties mentioned above were found in the literature and others were estimated, according to methods presented in Table 2. The T_b , critical properties and P_v were estimated by the modified Lydersen-Joback-Reid method [16].

The modeling of the vapor liquid equilibrium of the ternary system ethanol/water/IL was based on an asymmetric approach, in which the vapor phase was considered ideal and the liquid phase was considered not ideal; the activity coefficient was calculated with NRTL (Non Random Two Liquids) model. Studies presented in Table 1 show equilibrium data of the ternary system and thermodynamic parameters such as binary interaction parameters and non-random factor parameter.

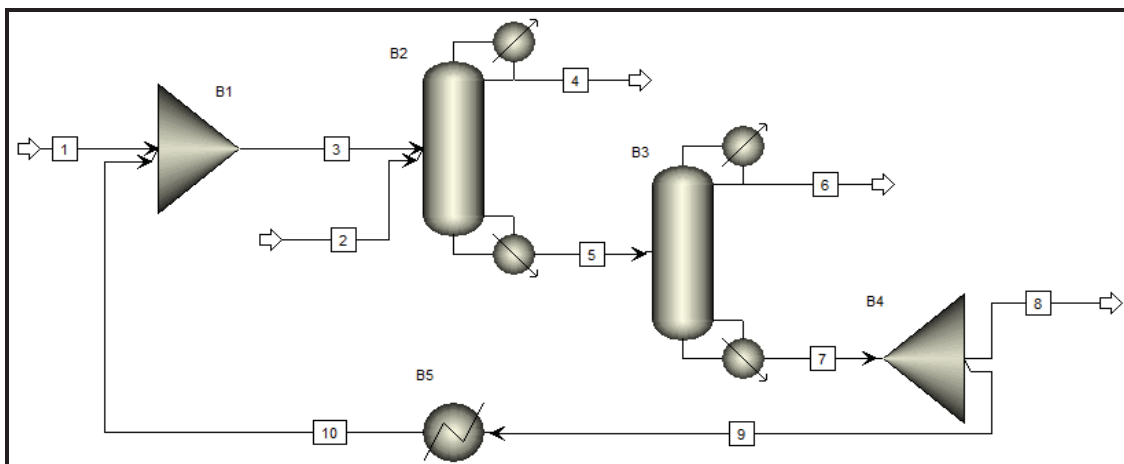


Fig. 1. Flowsheet of the extractive distillation process using Aspen Plus™. B1: mixer, B2: Ethanol Purification column, B3: IL Recovery Column, B4: Splitter and B5: Heat exchanger.

Table 2. Properties of selected ionic liquids

| Ionic Liquid | Molecular formula | Molar mass | Cp* [J/mol K] | ρ^* [kg/m ³] | Tb [K] |
|-----------------------------|--|------------|---------------------------------------|-------------------------------|--------|
| [bmim][Cl] | C ₈ H ₁₅ ClN ₂ | 174.67 | 327.4 [17] | 1080.0 [18] | 547.5 |
| [bmim][mSO ₄] | C ₉ H ₁₈ N ₂ O ₄ S | 250.32 | 375.0 [19] | 1196.3 [20] | 501.7 |
| [bmim][OAc] | C ₁₀ H ₁₈ N ₂ O ₂ | 198.26 | 383.2 [21] | 1053.0 [22] | 725.3 |
| [bmim][BF ₄] | C ₈ H ₁₅ BF ₄ N ₂ | 226.02 | 368.5 [23] | 1194.8 [24] | 438.9 |
| [bmim][N(CN) ₂] | C ₁₀ H ₁₅ N ₅ | 205.26 | 364.6 [25] | 1099.4 [25] | 650.3 |
| [emim][Cl] | C ₆ H ₁₁ ClN ₂ | 146.62 | Estimated by Kesler – Lee method [26] | 1186.0 [27] | 484.6 |
| [emim][BF ₄] | C ₆ H ₁₁ BF ₄ N ₂ | 197.97 | 306.8 [23] | 1222.3 [28] | 722.6 |
| [hmim][Cl] | C ₁₀ H ₁₉ ClN ₂ | 202.72 | Estimated by Kesler – Lee method [26] | 1040.4 [29] | 593.2 |

* At T = 298 K and P = 101.3 kPa

2.3. Process simulation

The process was simulated with a processing capacity of 500 m³/day at 101.3 kPa. The operation and design conditions were called input variables (InVar) and these were: Stream 1 temperature [K] and Stream 2 temperature [K], reflux ratio in columns B2 and B3, molar distillate rate [kmol/h] in columns B2 and B3, number of stages in columns B2 and B3, feed stage of column B2 and B3, feed stage of the IL in column B2, ethanol mass fraction in the feed stream and the mass ratio IL:Feed.

The output variables (OutVar) analyzed were chosen as representing the economic viability of the process. These were: heat duty (GJ/s) of column B2 and of column B3, the sum of heat duty of columns B2 and B3, the ethanol mass purity in the stream 4 and the water mass purity in the stream 6 and the recovery mass percent of ethanol and water.

Column model used was the RadFrac column available in the Aspen PlusTM. This model uses rigorous calculation, defined by the MESH equations (mass balances, equilibrium relationships, sum of compositions and enthalpy equations). The numerical solution was carried out simultaneously solving the MESH equations for the ternary system at each stage, using as numerical method the Broyden quasi-Newton method.

Initial conditions for input variables were based on the published work of extractive distillation processes using the separation mass agents as hyperbranched polymers [4], bioglycerol [30], [emim][DEP] [5], ethylene glycol and tetraethylene glycol [31]. Hence, simulations were computed with modifications on the initial conditions to achieve ethanol purity values higher than 0.995 (considering as stopping criterion).

3. Results and Discussion

In this study, the input variables were analyzed in order to satisfy the stopping criterion, confirming that in the studied process it was possible to obtain anhydrous ethanol. Values are reported in Table 3.

Table 3. Input variables used in each simulation with the respective IL studied

| InVar | [bmim] [Cl] | [emim] [Cl] | [bmim] [mSO4] | [emim] [BF4] | [bmim] [OAc] | [bmim] [BF4] | [bmim] [N(CN)2] | [hmim] [Cl] |
|--|----------------|----------------|------------------|-----------------|-----------------|-----------------|--------------------|----------------|
| Stream 1 temperature | 350 | 295 | 350 | 350 | 350 | 350 | 350 | 350 |
| Stream 2 temperature | 350 | 295 | 295 | 295 | 350 | 330 | 350 | 350 |
| Reflux ratio in the column B2 | 2.0 | 1.8 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Reflux ratio in the column B3 | 1.8 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Molar distillate rate in the column B2 | 332 | 330 | 330 | 340 | 340 | 338 | 340 | 340 |
| Molar distillate rate in the column B3 | 70 | 60 | 70 | 70 | 70 | 65 | 70 | 70 |
| Number of stages in column B2 | 27 | 33 | 33 | 33 | 33 | 30 | 33 | 33 |
| Number of stages in column B3 | 10 | 12 | 12 | 18 | 18 | 15 | 18 | 15 |
| Feed stage of column B2 | 19 | 26 | 20 | 28 | 26 | 29 | 26 | 28 |
| Feed stage of column B3 | 10 | 6 | 11 | 10 | 6 | 12 | 2 | 11 |
| Feed stage of the IL in column B2 | 2 | 6 | 6 | 19 | 6 | 4 | 2 | 11 |
| Ethanol mass fraction in the feed stream | 0.9000 | 0.8900 | 0.9300 | 0.9300 | 0.9300 | 0.9300 | 0.9300 | 0.9300 |
| Mass ratio IL:Feed | 2.500 | 0.970 | 0.500 | 0.500 | 0.500 | 0.095 | 0.350 | 0.100 |

As can be seen in Table 3, the used values of InVar were almost the same for all studied IL's. However, for the variables Molar distillate rate in the column B2, Feed stage of column B2, Feed stage of column B3, Feed stage of the IL in column B2 and Mass ratio IL:Feed it was not possible to use similar values for all IL's because the values of ethanol purities were lower than 0.995 (wt). Furthermore, with the simulations trials, it was possible to obtain anhydrous ethanol (ethanol purity higher than 0.995), using the different IL's. Figure 2 presents the required amounts of IL for ethanol dehydration.

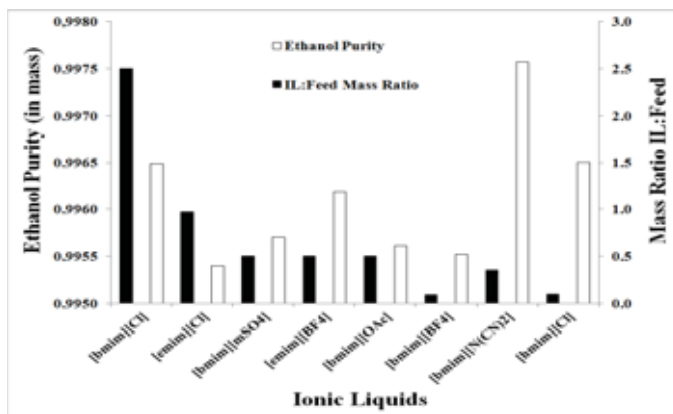


Fig. 2. Ethanol mass purity in the stream 4 and their respective Mass rate ratio IL: Feed obtained from simulations using different IL's

All IL's reached the anhydrous ethanol with purity higher than 0.995, using a mass ratio IL:Feed in the range of 0.095 to 2.5, which can be considered as acceptable values and presents a great potential in this type of separation process. However, in IL [bmim][Cl] and [Emim][Cl] case studies it is required a mass ratio IL:Feed of 2.5 and 0.97, respectively, constituting the highest amounts in the process.

In addition, studying the IL [bmim][N(CN)₂] it was possible to achieve an ethanol purity of 0.997 and using a mass ratio IL:Feed equal to 0.35, considered relatively low.

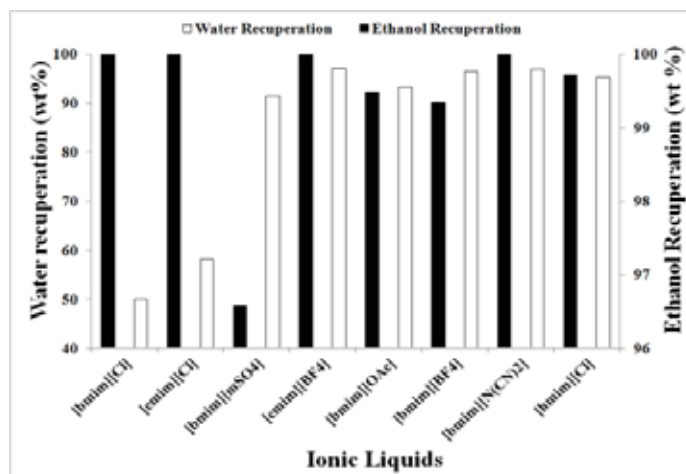


Fig. 3. Mass recovery percentage of the ethanol and water obtained from simulation

Figure 3 shows that with the most of IL's it is possible to get to recover the ethanol with high efficiency (about 100%) which it is important in this type of process assaying high product purities and efficient recoveries. On the other hand, based on the low IL's volatilities, using [bmim][mSO₄], [bmim][OAc], [bmim][BF₄], [bmim][N(CN)₂], [emim][BF₄], [hmim][Cl] it is possible to reach high water purification (>90 wt%).

Nevertheless, analyzing the [bmim][mSO₄] and considering a mass ratio IL:Feed equals 0.5 (Figure 2) it was pointed out that ethanol recovery only gets 96.6 wt% (Figure 3).

The reboiler duties of columns B2 and B3 and the sum of heat using different IL's is shown in Figure 4. The IL's [emim][BF₄] and [bmim][BF₄] had the highest heat duty sum of columns B2 and B3 with 149.56 and 134.39 GJ/s, respectively. The lowest heat duty sum of columns B2 and B3 was 46.70 GJ/s got through simulations using the IL [hmim][Cl].

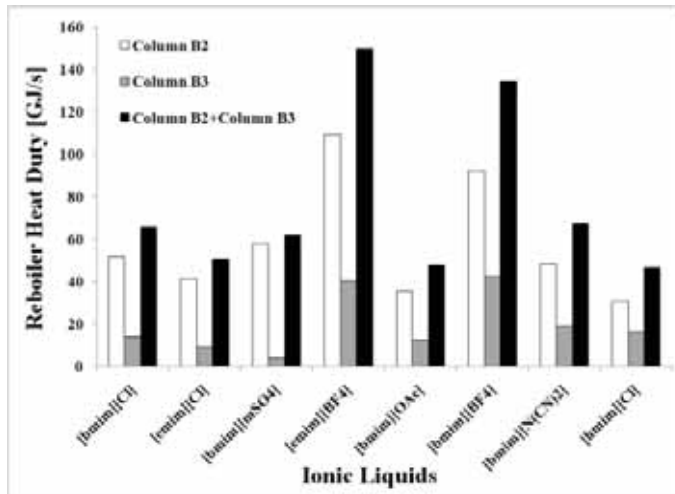


Fig. 4. Energy requirements on dehydration ethanol process

Figure 4 presents that heat duty in the reboiler of column B3 was always smaller than heat duty in the reboiler of column B2, the difference ranged from 6.62 % to 53.41 % for [bmim][mSO₄] and [hmim][Cl], respectively. This difference can be explained by the fact that the ethanol dehydration process occurs in this column.

Table 4 shows the comparison of the energy requirements using the different separating agents, comparing the values reported in the literature [1, 4, 30, 32-34] and the values found in this study. Hence, it is clear that the IL's have higher values than the others separating agents. It is possible to appreciate that [emim][BF₄] IL uses the most energy per kilogram of anhydrous ethanol obtained, and this value is about nine times higher than the required when glycerol is used.

The [hmim][Cl] was the IL that uses the least amount of energy, requiring 46.70 GJ/s for a kilogram of dehydrated ethanol (0.9300 to 0.9962 in mass) when compared with gasoline as conventional mass separation agent (Table 4).

The results of the simulations are not as attractive from the energetic point of view. Nevertheless, IL's bring great advantages related to the distilled products purity and high recovery percentages of ethanol, about 95 wt% as shown in Figures 2 and 3.

Table 4. Energy required to the ethanol dehydration process

| Mass separating agent | kJ / kg of anhydrous ethanol | Reference |
|-------------------------------------|------------------------------|--------------|
| Ethylene glycol | 1760 | [1] |
| Polyglycerol | 2094 | [4] |
| Glycerol | 1057 | [30] |
| Gasoline | 3180 | [32] |
| Ethylene glycol + potassium acetate | 3580 | [33] |
| Ethylene glycol + calcium chloride | 1425 | [34] |
| [bmim][Cl] | 4359 | In this work |
| [emim][Cl] | 3278 | |
| [bmim][mSO ₄] | 4118 | |
| [emim][BF ₄] | 9606 | |
| [bmim][Oac] | 3086 | |
| [bmim][BF ₄] | 8689 | |
| [bmim][N(CN) ₂] | 4334 | |
| [hmim][Cl] | 3008 | |

4. Conclusion

The extractive distillation process of ethanol + water mixture, using IL's was presented as a computational approach. The Aspen Plus™ process simulation environment was shown to be an appropriate tool for the study of the extractive distillation process, even in the condition where IL's are not found in the database of the simulator. This also shows the importance of data obtained from literature, as well as the choice of thermodynamic model for further modeling. Therefore, the process simulation showed the possibility of breaking the azeotrope in this mixture. IL's studied in this work use the mass ratio IL:Feed minimum of 0.095 for [bmim][BF₄] and maximum of 2.5 for the [bmim][Cl]. The minimum energy per kilogram of ethanol purified was 3008 kJ/kg anhydrous ethanol to [hmim][Cl]. On the other hand, the maximum energy per kilogram of ethanol purified was 9606 kJ/kg of anhydrous ethanol using [emim][BF₄]. The use of IL's as solvents in the ethanol dehydration process allows the production of high purity ethanol with recovery percentages above 96 wt%. The stream of water coming out of the process was also evaluated, finding that the water recovery is upper than 50 wt%, and free IL's.

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