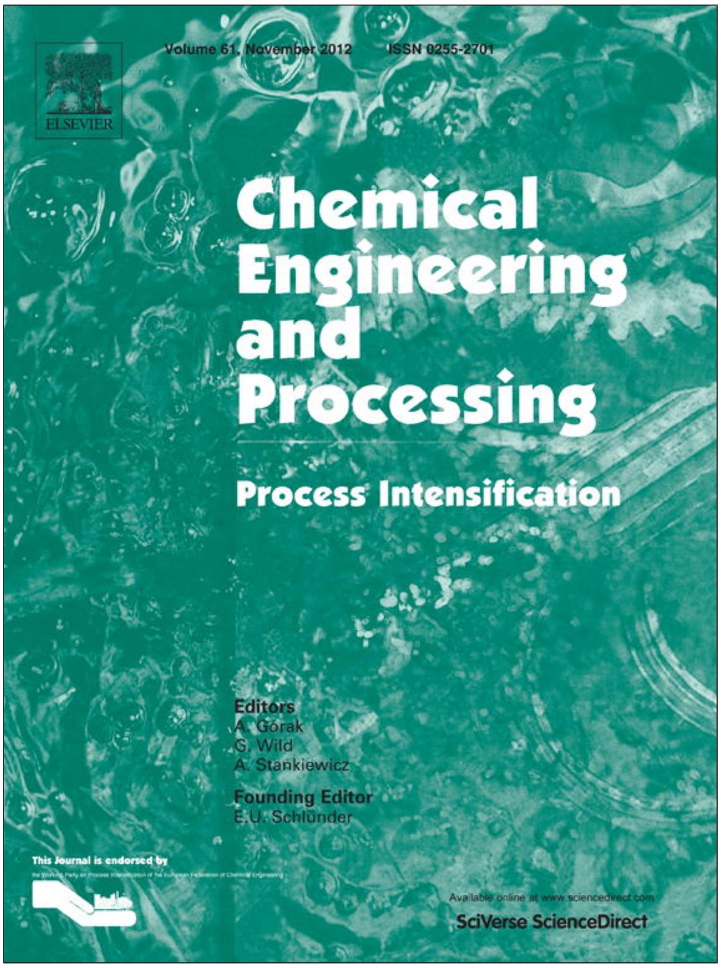
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Full Length Articles

Purification of bioethanol using extractive batch distillation: Simulation and experimental studies

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ABSTRACT

Among biofuels, bioethanol has increased in importance in many countries because it can be used directly or mixed with gasoline in combustion engines. The production of bioethanol in a fermentative process usually gives a dilute solution from which the bioethanol must be obtained in high concentration in order to be used as biofuel. The separation of an azeotropic mixture of ethanol and water using batch and semi-batch distillation was studied considering ethylene glycol and ionic liquids as entrainers. The simulation and experimental results indicate that the separation is favored using ethylene glycol in comparison to the use of ionic liquid; however, the ionic liquid is considered a green solvent and the use of ethylene glycol could be forbidden in the near future.

1. Introduction

During the past decade there has been a resurgence of interest and research in sources of renewable fuels and energy. Two major reasons for the increased interest are concerns about lowering carbon dioxide emissions from the burning of fossil fuels and oil supply insecurity. Biofuels produced from biomass, such as bioethanol, could provide alternative fuels for transportation. Biofuels are considered renewable because the biomass resources, from which they are produced, such as crops or other vegetation, can be regenerated within a relatively short time period. Ethanol can be made from a variety of sources including plant biomass, waste, and algae and has a long history of use as fuel for vehicles [1]. The annual bioethanol production capacity in the United States has reached 34 billion liters as of July 2008, exceeding the 2008 biofuel production mandate of 32 billion liters under the Energy Independence and Security Act (EISA). Under the EISA, conventional biofuel production will need to further increase to 57 billion liters by 2015. Currently, more than 95% of U.S. bioethanol is produced using corn [2]. Given this scenario it is necessary to generate clean and efficient processes for the production of bioethanol.

A typical mixture of a fermentation process can have up to 10% in weight of ethanol [3] from which can be obtained high purity ethanol using a simple distillation in order to obtain a mixture close to azetropic point (Fig. 1) followed by an extractive distillation column as indicated in Fig. 2. It is well known that distillation is the most used separation technique, but its high energy consumption is considered its main disadvantage, as a result other techniques are being explored, for instance, pervaporation. Despite the energy consumption required in distillation, it continues being the most important separation technique used in industrial practice.

Extractive distillation using ethylene glycol with or without salts like $CaCl_2$ as entrainer can be used [4], but it is necessary to explore the use of other entrainers that can be environmentally friendly. Recently Ravagnani et al. [5] have compared the energy demand of extractive distillation for the purification of ethanol using ethylene glycol and tetraethylene glycol as entrainers. They used tetraethylene glycol because it is expected that ethylene glycol could be forbidden due to its toxicity. However, the results indicate that the energy consumption is increased when tetraethylene glycol is used as entrainer.

In this work, the production of high purity bioethanol using ethylene glycol and ionic liquids (i.e., 1-butyl-3-methylimidazolium bromide) is explored using both simulation and an experimental batch distillation column. It is important to highlight that ionic liquids (ILs) are considered as green solvents that present advantages over classical solvents; for example, low vapor pressure, low toxicity and high decomposition temperature, but its cost is significantly higher than that of classical solvents like benzene, dodecane and others.

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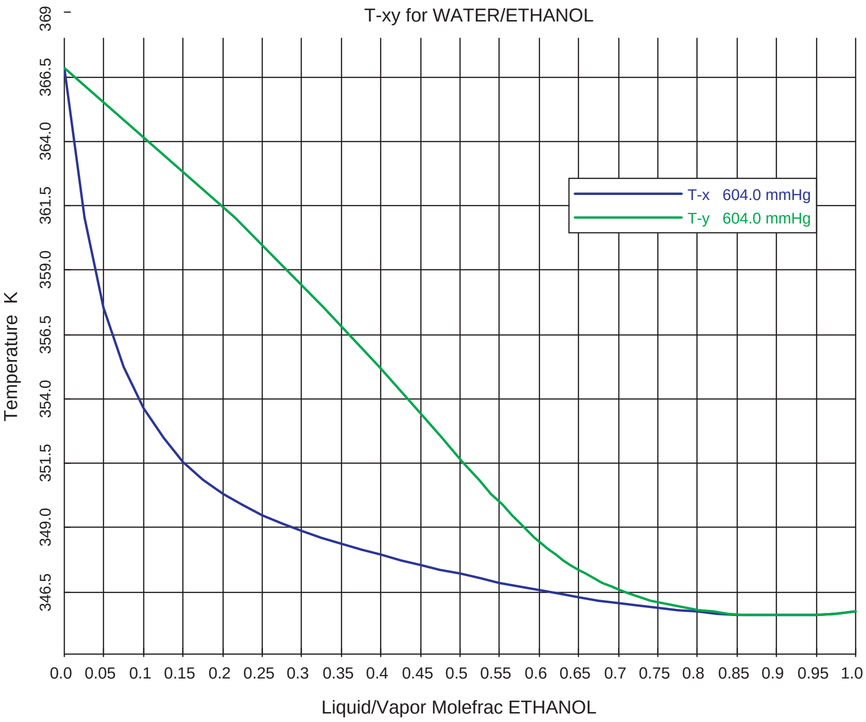

Fig. 1. Liquid–vapor equilibrium for ethanol–water at 604 mmHg.

2. Experimental equipment

The experimental batch distillation column is shown in Fig. 3. It contains five perforated plates, one reboiler and a total condenser. The distillation column is instrumented with four thermocouples in order to measure temperatures in the condenser, middle column, reboiler and distillated. The energy used in the distillation is supplied using an electric blanket.

3. Methodology

In the first part of the study, the simulation of the experimental batch distillation column was carried using the Batchfrac module of the process simulator AspenONE Aspen Plus. These simulations are carried out in order to reduce the experimental tests because of the high cost of the ILs. The NRTL model was used for representing the non idealities in the liquid phase. For the case of the ternary mixture ethanol–water–ethylene glycol the binary parameters were obtained directly for the database of the process simulator. For the mixture of ethanol–water–ionic liquid, experimental values of vapor–liquid equilibrium [6] were used in order to obtain the binary parameters required in the NRTL model since these values are not included in the database of the simulator AspenONE Aspen Plus. It is important to highlight that these binary parameters are obtained minimizing an error function using an optimization code.

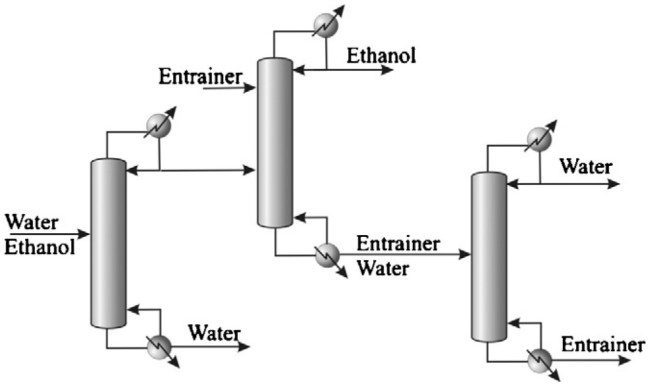

Fig. 2. Distillation sequence for purification of bioethanol.

Fig. 3. Experimental batch distillation column.

The effect of an ionic liquid on the nonideality of a solution can be determined using activity coefficients, which are obtained from phase equilibrium relations

$$\gamma_i = \frac{y_i \hat{\varphi}_i P}{x_i \varphi_{i,s} P_{i,s}} \tag{1}$$

where P is the vapor pressure of liquid mixture, $P_{i,s}$ is the vapor pressure of pure component i at system temperature, x_i and y_i represent the mole fraction of component i in the liquid and vapor phase, $\hat{\varphi}_i$ is the fugacity coefficient of component i in the vapor mixture, and $\varphi_{i,s}$ is the fugacity coefficient of pure component i in its saturated state, respectively. For a ternary system solvent (1) + solvent (2) + ionic liquid (3), the vapor phase is fully composed of solvent (1) and solvent (2) due to the negligible volatility of ionic liquid (i.e., $y_1 + y_2 = 1.0$). At low pressure, the vapor phase can be considered as ideal and taking into account the nonvolatility of ionic liquid, then Eq. (1) is reduced to

$$\gamma_i = \frac{y_i P}{x_i P_{i,s}} \quad i = 1, 2 \tag{2}$$

With these assumptions, the experimental activity coefficients (γ_i) for both solvents can be calculated from VLE data (i.e., x_i, y_i, T, P). Therefore, the NRTL parameters (Eqs. (3)–(8)) for modeling this ternary system (i.e., g_{ij}–g_{jj} and α_{ij}) have been obtained by the fitting of the experimental activity coefficients of both solvents using a least squares formulation. The objective function used for parameter estimation was defined as Eq. (9).

$$ln\gamma_i = \frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} + \sum_j \frac{x_j g_{ij}}{\sum_k x_k g_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} g_{mj}}{\sum_k x_k g_{kj}} \right) \tag{3}$$

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \tag{4}$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} \tag{5}$$

$$\alpha_{ij} = c_{ij} \tag{6}$$

$$\tau_{ii} = 0 \tag{7}$$

$$g_{ii} = 1 \tag{8}$$

$$F_{\text{obj}} = \sum_{i=1}^{2} \sum_{j=1}^{\text{ndat}} \left(\frac{\gamma_{ij}^{\text{exp}} - \gamma_{ij}^{\text{calc}}}{\gamma_{ij}^{\text{exp}}} \right)^2 \tag{9}$$

where γ_i^{exp} and γ_i^{calc} are, respectively, the experimental and calculated values for the activity coefficient of component i and ndat is the overall number of experimental data.

This objective function was globally optimized with respect to nine NRTL parameters. Note that in the modeling of vapor–liquid equilibrium data with and without ionic liquids, the parameter estimation problems usually have non-linear and non-convex solution spaces. In fact, this optimization problem is complex in nature and difficult to solve using traditional local optimization methods due to the presence of several local minima for the objective function used as the optimization criterion. In process design, the failure to find the globally optimal parameters for a thermodynamic model may cause errors and uncertainties. Therefore, reliable optimization methods should be used for this purpose. Several studies have shown the potential of stochastic optimization methods to solve parameter estimation problems for the modeling of vapor–liquid equilibrium (e.g., Bonilla-Petriciolet et al. [7]). These methods offer several advantages for solving global optimization problems such as generality, reliability and robust performance, little information requirement for the optimization problem to be solved, easy implementation, and reasonable computational requirements. Thus, in the present study we have used the simulated annealing stochastic optimization method for reliably determining the parameters of NRTL model. The algorithm parameters used for simulated annealing are reported in Bonilla-Petriciolet et al. [7]. The binary parameters for the NRTL obtained through the optimization procedure are contained in Table 1.

Table 1
Binary parameters of the NRTL model obtained for the mixture of ethanol, water and 1-butyl-3-methylimidazolium bromide.

i	Ethanol	Ethanol	Water
j	Water	Ionic liquid	Ionic liquid
a_{ij}	0	0	0
a_{ji}	0	0	0
b_{ij}	−192.917158	−2716.683474	−3565.281031
b_{ji}	824.6228752	−830.9568853	−849.5646663
c_{ij}	0.196485	0.202258	0.105651

The dynamic model used in Batchfrac contains transient total mass balance, transient component mass balances, equilibrium relationship, summation constraints and transient energy balance for each equilibrium stage. This dynamic model can be solved using integration techniques implemented in the process simulator; for example, Euler or Runge–Kutta methods.

The mixture of ethanol and water (85% in mass of ethanol) was introduced in the reboiler of the distillation column, this composition can be obtained using ordinary distillation of a typical mixture of fermentation of sugarcane bagasse [8–10], and ethylene glycol or IL was feed in the reboiler. Several values of the ratio of azeotropic mixture to entrainer, reflux ratio and distillate rate were tested in order to know the behavior.

When the ternary mixture is charged in the reboiler, the heating was switch on and the cooling water is used in the condenser. First, operation in the fashion of total reflux was used until the temperature profile remains constant and second reflux ratio and distillate rate were set for the batch operation. This operation is common in batch distillation and is implemented in the process simulator.

In the second stage of the study, experimental tests were carried out using total reflux operation because at this stage of the research, the main objective is to achieve a composition of ethanol higher to the composition of the azetropic point. Experimental studies were carried out using pure ethylene glycol, pure ILs and mixtures of ethylene glycol and ILs as entrainers.

4. Simulation results

In the first part of the study, simulation results were generated for the purification of bioethanol using both ethylene glycol and ILs as entrainers.

5. Ethylene glycol as entrainer

The results presented in Fig. 4 correspond to the charge of a mixture of ethanol and water (85% in mass of ethanol) in the batch distillation column operated at atmospheric pressure (604 mmHg). Both the azeotropic mixture and entrainer were feed into the reboiler of the column.

Fig. 4 shows that the ratio (mole base) of ethylene glycol to feed plays an important role in the composition of the distillate. For values around 1 of this ratio, it is impossible to achieve a composition of the ethanol superior to the azeotropic composition, but as the ratio increases the composition of the distillation increases to values higher than that of the composition of the azeotropic mixture. It is important to note that the composition reaches a maximum and then diminishes as the distillation proceeds. The maximum value obtained in the distillated depends on the ratio of entrainer/feed, increasing as this ratio does.

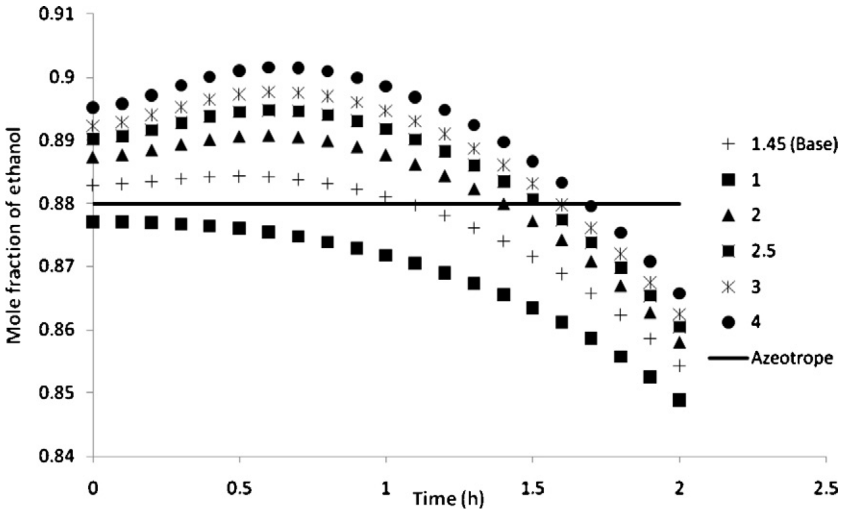

Fig. 4. Effect of the ratio ethylene glycol/feed on the composition of the distillate.

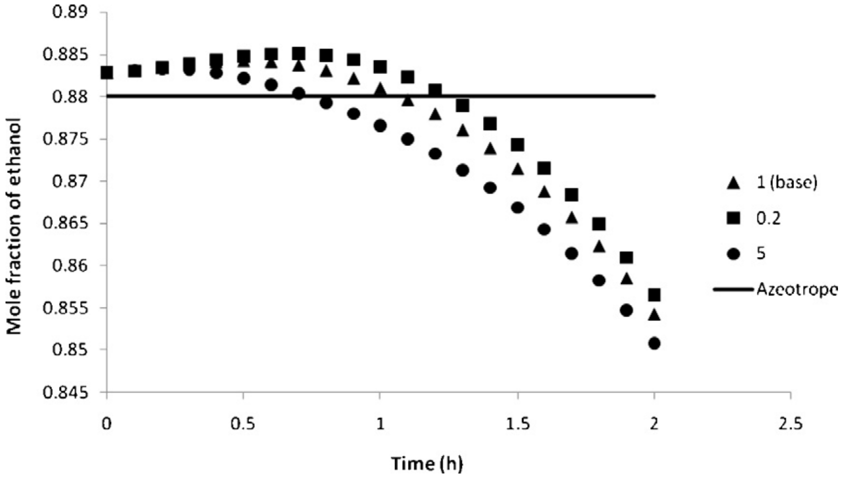

Fig. 5. Effect of the ratio reflux ratio on the composition of the distillate.

According to Fig. 4, the composition of the distillate can be maintained above of the composition of the azeotropic point for a longer period of time when the ratio of entrainer/feed is increased.

The effect of the reflux ratio on the mole fraction of ethanol in the distillated is presented in Fig. 5. According to this figure, for a short period of time the composition of the ethanol in the distillate does not depend on the reflux ratio, but as the time proceeds the composition of the ethanol diminishes when the reflux ratio increases.

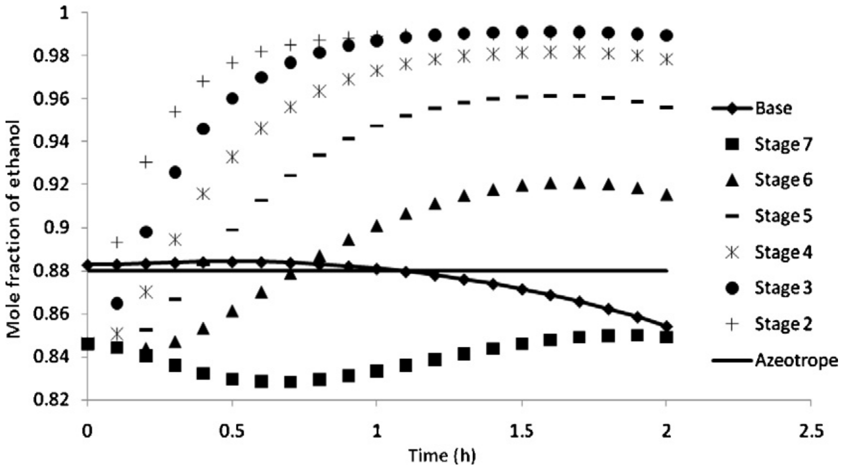

Fig. 6. Effect of the feed stage of the entrainer on the composition of distillate.

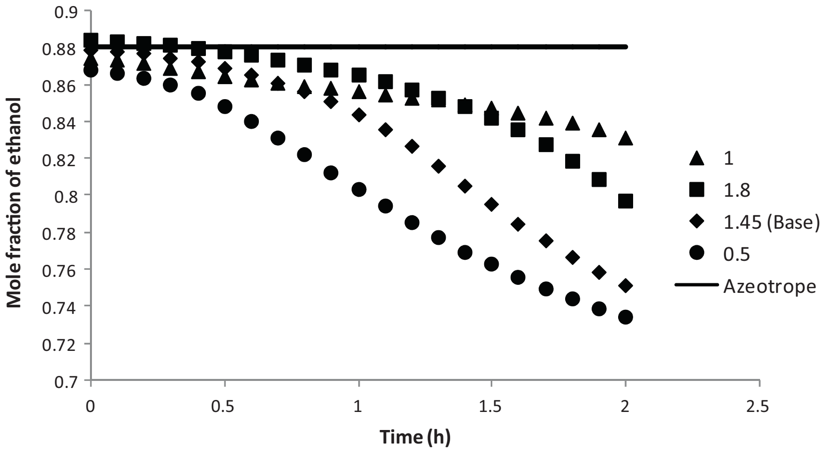

Fig. 7. Effect of the ratio ionic liquid/feed on the composition of the distillate.

The distillation column can be operated at semi-batch fashion when the azeotropic mixture is introduced in the reboiler and the entrainer is feed continuously in other stage. Fig. 6 presents the results for different feed stages and it can be seen in comparison to the results presented in Fig. 4 that the separation is improved since higher composition of ethanol can be obtained during a longer period of time. This is possible because the entrainer is feed close to the top of the distillation column and more contact is achieved between the entrainer and the ethanol–water mixture. In contrast, the results presented in Fig. 4 correspond to the case where both entrainer and ethanol–water mixture are introduced into the reboiler of the distillation column.

Also, the separation is favored as entrainer is introduced in the stages close to the condenser.

6. Ionic liquid as entrainer

When the distillation column was analyzed considering ionic liquid as entrainer for batch and semi-batch operations, the simulation required the use of the binary parameters contained in Table 1. The results presented in Figs. 7 and 8 indicate that composition of the distillate is above of the composition of the azeotrope only for high values of the ratio of ionic liquid/feed and for the feed of the entrainer near to the top of the distillation column. It is important to mention that the separation is favored using ethylene glycol, but ethylene glycol could be forbidden in the next years as indicated in Ravagnani et al. [5]. Additionally, the separation using ionic liquid requires significantly higher amounts of entrainer for achieving the purity in the ethanol that can be translated into higher amount of energy required in the reboiler and more traffic of liquid and vapor, i.e., increment in the diameter of the distillation column. The last two aspects impact in a higher total annual cost using ionic liquid in contrast to the use of ethylene glycol as entrainer.

7. Experimental results

For the experimental runs, the model mixture of ethanol and water (85% in mass of ethanol) was prepared using high purity ethanol from Sigma–Aldrich. Also, the entrainers: ethylene glycol, 1-butyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride were provided by Sigma–Aldrich. For this stage, the mixture of ethanol–water and the entrainer were introduced in the reboiler and the heater was switched on. When the steady-state was reached at total reflux, a distillate sample was removed and the composition was inferred using the refraction index. The entrainers for the experimental runs are described in Table 2. According to Fig. 9, the experimental results are in agreement with those obtained using simulations. The experimental

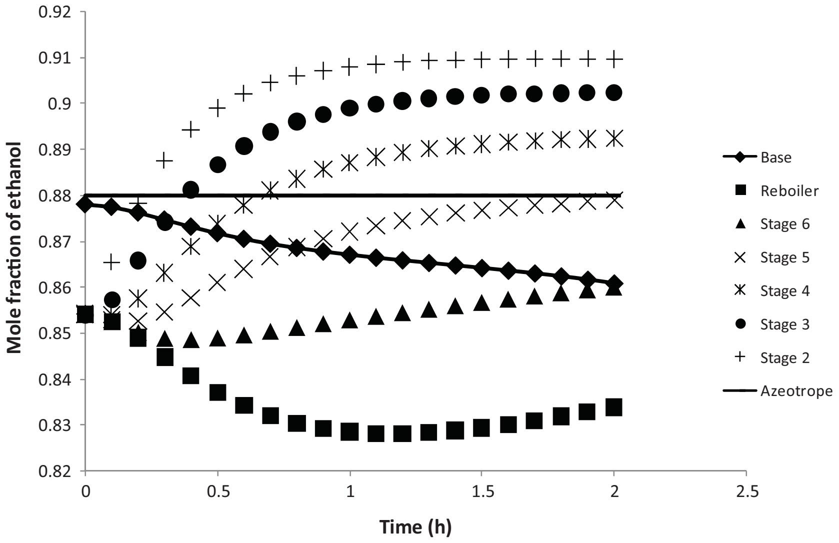

Fig. 8. Effect of the feed stage of the entrainer on the composition of distillate.

Table 2
Entrainers used in the experimental tests.

Case	Entrainer
1	5 g of 1-butyl-3-methylimidazolium chloride dissolved in ethylene glycol
2	5 g of 1-butyl-3-methylimidazolium bromide dissolved in ethylene glycol
3	Pure ethylene glycol
4	20 g of 1-butyl-3-methylimidazolium chloride dissolved in ethylene glycol
5	20 g of 1-butyl-3-methylimidazolium bromide dissolved in ethylene glycol
6	5 g of pure 1-butyl-3-methylimidazolium chloride
7	5 g of pure 1-butyl-3-methylimidazolium bromide

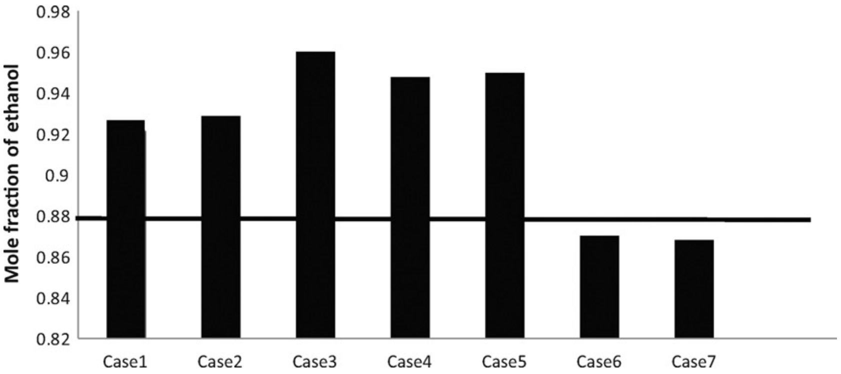

Fig. 9. Experimental results.

results indicate that in fact the use of ethylene glycol conducts to higher compositions than using ILs. The results obtained using ILs are better only using high concentrations of ILs, for instance 10% (mass percent), but it is important to highlight that the ILs are very expensive in contrast to that of the ethylene glycol. At this moment, although these results might be demotivating, since the use of ILs presents good results only using considerable amounts in order to overcome the azeotropic point, conducting to higher total annual costs in contrast to the use of conventional solvents, but advances in the synthesis of the ILs could reduce the production cost in the near future [11]. Also, some advanced operational techniques for batch distillation, for instance, cyclic operation, could be explored [12].

8. Conclusions

The production of high purity ethanol from a typical mixture of ethanol–water from a fermentation process has been studied considering batch and semi-batch distillation. Ethylene glycol and ionic liquids were used as entrainers for the extractive distillation column. The separation is favored using ethylene glycol as entrainer in comparison to use the ionic liquid. However, the ionic liquid is considered as green solvent, the cost of the use of ILs is higher than that of conventional entrainers.

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