ESTUDO DE UMA NOVA ESTRATÉGIA PARA A PRODUÇÃO DE ETANOL ANIDRO EM USINAS DO RIO DE JANEIRO: ADIÇÃO DE PROPILENOGLICOL COMO CO-SOLVENTE

ESTUDIO DE UNA NUEVA ESTRATEGIA PARA LA PRODUCCIÓN DE ETANOL ANHIDRO EN LAS PLANTAS DE RÍO DE JANEIRO: ADICIÓN DE PROPILENGLICOL COMO CODISOLVENTE

STUDY OF A NEW STRATEGY FOR THE ANHYDROUS ETHANOL PRODUCTION IN UNITS IN RIO DE JANEIRO: ADDITION OF PROPYLENE GLYCOL AS COSOLVENT

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Resumo

A produção de etanol anidro, devido à presença do azeótropo, é difícil utilizando a destilação convencional, sob pressão atmosférica, como processo de separação. Portanto, um dos métodos utilizados é a destilação extrativa, que consiste na adição de uma terceira substância capaz de alterar o equilíbrio líquido-vapor do sistema, obtendo assim a desidratação de etanol. Portanto, o processo de separação do etanol foi avaliado, usando propilenoglicol como solvente, usando o software ProSimPlus. A simulação foi realizada variando as proporções solvente/alimentação (S/F) em 0,5, 0,7 e 0,9 em peso. Os resultados mostraram que o azeótropo foi quebrado, obtendo a mesma fração de etanol nas três razões estudadas. Assim, optou-se pela menor razão S/F (0,5) para medir o equilíbrio líquido-vapor do sistema ternário, variando a concentração molar de etanol de 0,2 a 0,9. Os dados experimentais foram medidos em triplicata em um ebuliômetro semelhante ao de Othmer e as análises das amostras foram realizadas em um densímetro digital. Os resultados experimentais obtidos mostraram que o azeótropo foi quebrado, validando os resultados obtidos na simulação, confirmando que o propilenoglicol é um solvente promissor para a produção de etanol anidro, e pode ser aplicado em usinas de álcool presentes no Rio de Janeiro.

PALAVRAS CHAVE: Simulação de processo; Etanol anidro, Azeótropo; Propilenoglicol.

Resumen

La producción de etanol anhidrodebido a la presencia del azeótropo se dificulta usando ladestilación convencional a presión atmosférica, como proceso de separación. Uno de los métodos utilizados es ladestilaciónextractiva, que consiste enlaadición de una tercerasustancia capaz de alterar elequilibrio líquido-vapor del sistema, obteniendoasíladeshidratacióndel etanol. Así, elproceso de separación de etanol se evaluó usando propilenglicol como solvente empleandoel software ProSimPlus. La simulación se realizó variando larelación solvente/alimentación (S/F) en 0,5, 0,7 y 0,9 en peso. Los resultados mostraron que el azeótropo se rompió, obteniendolamismafracción de etanol enlastres proporciones estudiadas. Así, se eligiólarelación S/F más baja (0,5) para medir elequilibrio líquido-vapor del sistema ternario, que varío desde una concentración de etanol de 0,2 a 0.9 molar. Los datosexperimentales se midieronen triplicado enunebullómetro tipo Othmer y losanálisis se realizaronenun densímetro digital. Los resultados experimentalesmostraron que el azeótropo estaba roto, validando los resultados de lasimulación, confirmando que elpropilenglicol es un solvente prometedor para laproducción de etanol anhidro y se puede aplicar en plantas de alcohol presentes en Río de Janeiro.

PALABRAS CLAVE:Simulación de procesos; Etanol anhidro, azeótropo; Propilenglicol.

Abstract

The production of anhydrous ethanol, due to the presence of the azeotrope, is difficult using conventional distillation, at pressure atmospheric, as a separation process. One of the methods used is the extractive distillation, consisting in the addition of a third substance capable to change the vapor-liquid equilibrium of the system and obtaining the dehydration of ethanol. Therefore, the ethanol separation process using propylene glycol as solvent was evaluated using the ProSimPlus software. The simulation was done varying the solvent/feed ratios (S/F) in 0.5, 0.7 and 0.9 by weight. The results showed that the azeotrope was broken, obtaining the same ethanol fraction in the three ratios studied. Thus, it was chosen the lower ratio S/F (0.5) to measure the vapor-liquid equilibria of the ternary system, varying the molar concentration from 0.2 to 0.9. The experimental data were measured in triplicate in a similar Othmer'sebuliometer and the analyses of the samples were done in a digital densimeter. The experimental results showed that the azeotrope was broken, validating the results obtained in the simulation, confirming that the propylene glycol is a promising solvent for the production of anhydrous ethanol, and can be applied in the ethanol units present in Rio de Janeiro.

KEYWORDS: Process simulation; Anhydrous ethanol; Azeotrope; Propylene glycol.

1. Introduction

The search for alternative and renewable sources of energy has become a global concern, due to the negative impacts on the environment by the excessive use of fossil fuels (Pinzi*et al*., 2014). Ethanol, like biodiesel, has been treated as a promising alternative to replace fossil fuels, being a clean-burn fuel, which reduces the emission of gases into the atmosphere (Souza *et al.,* 2013).

The ethanol, as a fuel, has two applications, in its hydrated and anhydrous form. The anhydrous ethanol is used as a gasoline additive and approximately 20-25% is added to the gasoline. According to the ANP (2010) (Brazilian National Oil Agency), the ethanol for this use must contain at least 99.6% of alcohol. However, due to the presence of azeotrope in the ethanol-water system (88% molar), it is not feasible the separation of the ethanol, at normal pressure, using conventional distillation (Soares, 2010).

Thus, the separation of the ethanol-water mixture is essential and other methods have been required for such process. The extractive distillation has been considered an alternative method for anhydrous ethanol production due to the low energetic consumption and operational costs (Souza, 2012). The process occurs in the presence of a non-volatile and high boiling point solvent, known as separating agent, which is added to the azeotropic mixture with the objective to modify the relative volatility of the original mixture, promoting the dehydration of ethanol (Gil *et al.,* 2008).

The choice of the solvent to be used as a separating agent should be done in order to minimize the production costs, and to provide the desired separation by employing a minimum amount of solvent. It is important to add that the solvent must have a low vapor pressure, a good affinity with water and do not present azeotrope with the system components (Soares, 2010).

Different separation agents have been proposed, as salts (Soares *et al.,* 2014; Jurado *et al*., 2017), ionic liquids (Zhao *et al.,* 2006; Silva, 2016) and liquid solvents such as ethylene glycol and glycerol (Pla-Franco *et al*., 2013; Souza *et al.,* 2013). The search for non-toxic and non-corrosive solvents is necessary in order to obtain cleaner processes, making them economic and effective in many azeotropic separations.

In this way, this work has the motivation to use the propylene glycol as a separation agent. Propylene glycol is a non-toxic compound and can be produced from the conversion of glycerol, a byproduct of biodiesel production, being considered a green solvent, given its renewable source.

An important step in the process is the prior characterization of the mixture to be separated. Thus, in the present study, the influence of the propylene glycol on the vapor-liquid equilibrium of the ethanol-water system, at atmospheric pressure, will be evaluated through ProSimPlus software. With the best result obtained, measurements will be made of vapor-liquid equilibrium data at atmospheric pressure at different molar concentrations.

The ethanol-water-propylene glycol system has no equilibrium data available in the literature. The phase equilibrium knowledge is essential for the project and design of the separation processes because equilibrium data establishes the exact conditions of temperature and pressure and consequently, the compositions of the components.

2. Methodology

2.1. Process Simulation

The thermodynamic model applied to represent the vapor-liquid equilibrium data of the ternary system containing ethanol - water - propylene glycol was chosen in the ProSimPlus software. The

Raoult's law modified with γ-Φ approach was used to represent the vapor-liquid equilibrium of the system.

The activity coefficient (γ) was considered to better represent the non-ideality of the liquid phase, being calculated by the thermodynamic model NRTL. The vapor phase was considered ideal (Φ=1) because the distillation will occur under at atmospheric pressure (Smith *et al.,* 2007). Thus, the equation 1 can be written.

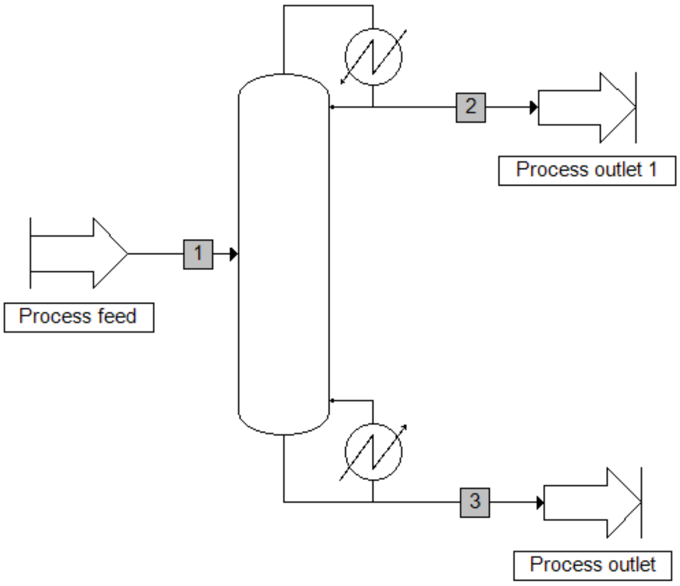
$$y_i P = x_i \gamma_i P_i^{sat} \qquad (1)$$

The vapor-liquid equilibrium curves were generated for the ethanol-propylene glycol and water-propylene glycol systems to check the existence of an azeotrope, and to enable the use of propylene glycol as a separating agent in the ethanol-water extractive distillation process.

The short-cut distillation column was considered for the process simulation, which uses the project calculation method of Fenske, Underwood and Gilliland. This method aims to obtain an initial estimate of the number of equilibrium stages (N), feeding location (NF) and operating limit conditions: minimum reflux ratio (Rmin) and minimum number of stages (Nmin).

Based on the work of Merenda e Furter (1974), liquid separating agents are generally present between 50 and 90% by weight of the liquid phase. Thus, The S/F (solvent/feed) ratio was varied from 0.5, 0.7 and 0.9 by weight for the simulation of the distillation process of ethanol-water-propylene glycol. Figure 1 shows an illustrative schematic of the simulated process presented by the simulator.

Figure 1. Illustrative diagram of the simulation process of the extractive distillation, 1 – feeding stream of the mixture (ethanol, water and propylene glycol), 2 – distillate stream (anhydrous ethanol), 3 – bottom stream (water and propylene glycol).



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2.2. Chemicals

Propylene glycol (99.8% minimum purity, supplied by Vetec, Rio de Janeiro, Brazil), absolute ethanol (minimum 99.8% purity, supplied by Proquímios, Rio de Janeiro, Brazil) and distilled water were used to prepare the mixtures.

2.3. Experimental Procedure

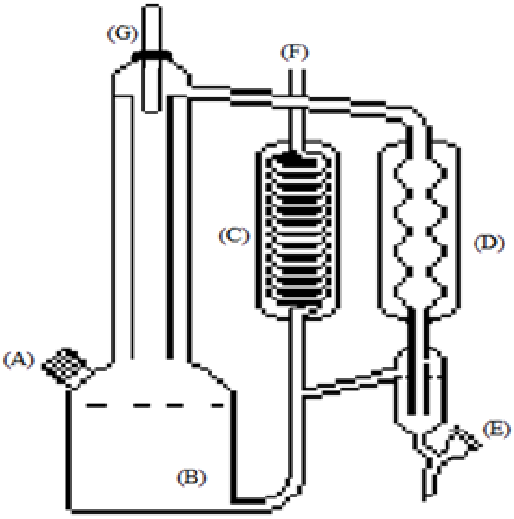
The experimental procedure was conducted in an Othmer's type ebulliometer, shown in Figure 2. This ebulliometer is made of borosolicate glass, with a total reflux and full capacity of 300 mL. It consists of an equilibrium cell, two condensers and two outputs for sampling the liquid and vapor phases. There is an opening in the coil condenser to ensure atmospheric pressure. The temperatures of the liquid and vapor phases were measured by digital thermometer. This ebulliometer has been previously tested in other studied and already published works, involving the systems as ethanol-water-glycerol (Souza *et al.,* 2013) and ethanol-water-1-ethyl-3-methyl imidazole chloride (Silva, 2016).

The experimental procedure begins with the feeding of an ethanol, distilled water and propylene glycol mixture with a specific composition. A magnetic stirrer is used to ensure the homogeneity of the solution. After the circulation of water through the boiling condensers begins, the heating is promoted and the ebulliometer is coated with insulating material to minimize heat losses. The bubble temperature was monitored at every intervals of 10 min, and the equilibrium was established when the temperature remained stable for 30 minutes.

The liquid-vapor equilibrium data were measured in triplicate at constant atmospheric pressure, varying molar ethanol concentrations from 0.2 to 0.9 and solvent / feed ratio (S/F) of 0.5 wt., considering this value as the best result obtained in the simulation process. The vapor phase samples were then collected and analyzed.

Figure 11. Schematic diagram of the ebulliometer used in this work. (A) Temperature measurement and sampling of liquid phase, (B) equilibrium cell, (C) secondary condenser, (D) primary condenser, (E) vapor phase sampling port, (F) external

opening, (G) temperature of the vapor phase.



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2.4. Sample Analysis

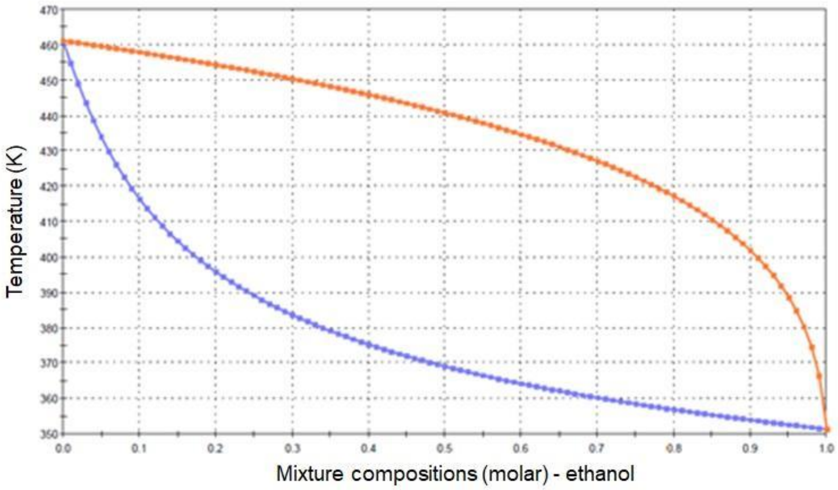
Sample compositions were determined with the experimental measurements of specific mass, obtained using a digital densimeter (GEHAKA, DSL 920 model), with ±0.0001 g/cm^3 of uncertainty. A calibration curve was previously constructed with ethanol–water mixtures of known mole composition. All the measurements were done in triplicate. The calibration curve obtained was used to determine the ethanol mole fraction of the samples.

3. Results And Discussion

Figures 3 and 4 show the liquid-vapor equilibrium curves generated by the ProSimPlus simulator for the binary systems of ethanol-propylene glycol and water-propylene glycol. These results are important because it is possible to observe that there is not the presence of an azeotrope between them. According to Souza (2012), in the extractive distillation process, the added solvent should not form another azeotrope in the system. Thus, the choice of propylene glycol as an extracting agent of the ethanol-water system became possible.

Therefore, the simulation was done choosing the short-cut column. Table 1 presents the simulation data obtained for the different ratios studied. It can be seen that for all the simulations, a distillate of 0.994 molar of ethanol was obtained, independently of the S/F ratio. Thus, the use of propylene glycol can be considered efficient for the extractive distillation of the ethanol-water system, since it enabled the azeotrope breakage in the three ratios analyzed.

FigureIII. Vapor-liquid equilibrium of the ethanol-propylene glycol system.



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FigureIV. Equilibrium curve of the water-propylene glycol system.

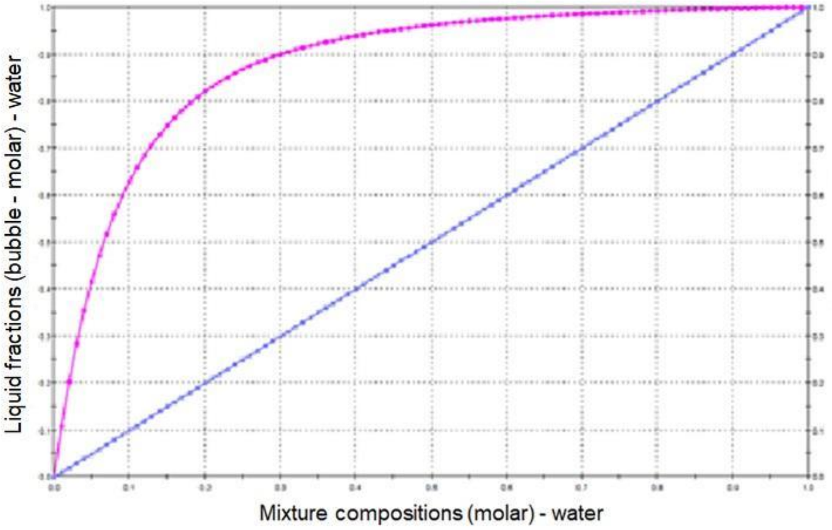

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Table 1. Simulation results of the extractive distillation process of the ethanol-water-propylene glycol system.

Components	**Molar fraction (distillate)**		
	S/F=0.5	**S/F=0.7**	**S/F=0.9**
Ethanol	**0.994**	**0.994**	**0.994**
Water	**0.006**	**0.006**	**0.006**

Propylene glycol	0.0	0.0	0.0

The absence of the presence of propylene glycol was expected, due to the high boiling point of the extracting agent, proving that the azeotrope was broken inside the column.

Table 2 shows the effect of each S/F ratio, minimum reflux ratio and energy consumption on the molar composition of the distillate in the extractive column. The best operational condition was given by the simulator, with a ratio of R/Rmin equal to 1.3. It can be observed that with the increase of the S/F ratio, there is an increase in the energy consume, which makes the use of S/F equal to 0.5 more favorable.

Table II. Operating conditions for the different S/F ratios.

S/F	R/R_{min}	Reflux Ratio	Condenser Duty (kcal/h)	Reboiler Duty (kcal/h)
S/F=0.5	1.3	2.502	282104	348345
S/F=0.7	1.3	3.503	362725	500318
S/F=0.9	1.3	4.715	460297	1.0169E^{06}

Therefore, the vapor-liquid equilibrium data measurements were performed for the ternary ethanol-water-propylene glycol system, using the S/F ratio = 0.5. Table 3 presents the experimental results of temperature and vapor phase composition of the ethanol-water-propylene glycol system, as well as with their respective standard deviations. The uncertainties of the measured variables regarding solvent-free ethanol (x') composition were 0.006 for the vapor phase molar fraction (y), and 0.1 K for the temperature (T). The calculation of uncertainties was taken from the work of Baratto et al. (2008). The presented values are the mean of the experimental data measured in triplicate.

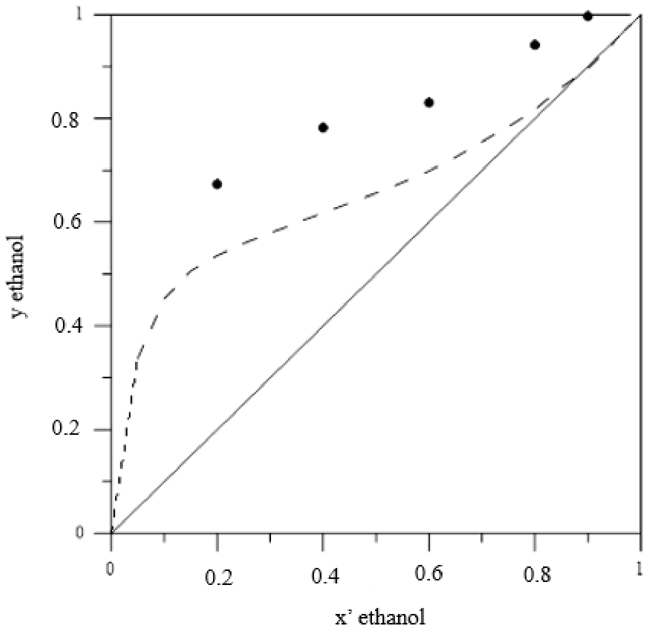
Table III.Data for the vapor-liquid equilibrium measurements of the ethanol-water-propylene glycol system.

x' ethanol	S/F= 0.50			
	T (K)	y ethanol	Standard Deviation (T)	Standard Deviation (y)
0.20	358.63	0.6728	2.17E^{-01}	1.46E^{-03}
0.40	354.58	0.7820	3.60E^{-01}	1.36E^{-04}
0.60	352.99	0.8301	1.25 E^{-02}	2.25E^{-03}
0.80	352.16	0.9415	1.23E^{-01}	2.91E^{-03}
0.90	352.09	0.9968	1.34E^{-01}	2.47E^{-03}

Figure 5 shows the vapor-liquid equilibrium curve of the ternary system, with the data measured in this work. Data from the binary ethanol-water system (Gmehling*et al.*, 1981) were also presented for a better comparison the influence of propylene glycol. The propylene glycol used modifies the behavior of the vapor-liquid equilibrium curve in a positive way, allowing the azeotrope to "breakage", leading to greater ethanol dehydration. Thus, the results obtained in the simulation were validated.

Some authors had proven the efficiency of the extractive distillation methods using different solvents for ethanol dehydration. Souza *et al*. (2013) performed the equilibrium data measurements for the ternary system of ethanol-water-glycerol with 50, 70 and 90 wt% of solvent. For all the concentrations of the solvent, it was not observed the presence of the azeotrope. Lai, Lin and Tu (2014) evaluated the influence of 1,3-propanediol on the ethanol-water system at concentrations of 10, 30 and 50%. It was found that the use of 50 wt% of 1,3-propanediol eliminated the azeotropic system. In this way, it was also possible to affirm that the propylene glycol was efficient, due to the breakage of the azeotrope.

FigureV. Vapor-liquid equilibrium of the ethanol-water-propylene glycol ternary system: ----: binary ethanol-water system (Gmehling*et al.*, 1981); ●: S/F=0.50.



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According to Silva (2016), when the affinity of the solvent is lower with ethanol, the relative volatility (α_{12}), increases, indicating that the azeotrope of the ethanol-water mixture can be broken. Moreover, the separation factor of the mixture also increases with the increase of value of α_{12}. Based on the results obtained from the compositions, the relative volatility of ethanol in water (α_{12}) was calculated using equation 2.

$$\alpha_{12} = \frac{\frac{y_1}{x'_1}}{\frac{y_2}{x'_2}} \qquad (2)$$

Table 4 presents the variation of the relative volatility with the liquid phase molar fraction of ethanol. It can be seen that, for higher molar fractions of ethanol, the α_{12} values were higher than 1, also confirming the applicability of propylene glycol for the azeotrope breakage. The higher value observed in Table 4 was obtained in the solution with higher molar composition of ethanol, showing the total solvation of water molecules by those of propylene glycol.

Table IV.Relative volatilities of the ethanol-water-propylene glycol system for S/F ratio=0.5.

x' ethanol	**Relative volatility (α_{12})**
0.20	**8.22**
0.40	**5.38**
0.60	**3.25**
0.80	**4.02**
0.90	**34.61**

4. Conclusions

The experimental results of the measurement of the vapor-liquid equilibrium of the ternary system ethanol-water-propylene glycol corroborated the previous simulation study. According to the results of the simulation, the S/F ratio of 0.5 was enough to break the azeotrope between ethanol and water. The variation of the solvent/feed (S/F) ratio did not interfere in the results, obtaining the same fraction of ethanol in the three ratios, whereas the use of S/F=0.5 was the most viable, due to the lower solvent consumption and for achieving the composition of the distillate with lower energy consumption.

Moreover, new vapor-liquid equilibrium data for this ternary system were generated, enriching the literature. The data showed that the use of propylene glycol as a third component to be applied in a distillation process is promising and technically feasible for ethanol dehydration.

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