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Simulation of the Extractive Distillation Process of Ethanol-Water-Propylene Glycol System

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Abstract

Anhydrous ethanol is of great importance in the chemical industry, due to its diversity of applications, fuel being the main one. Anhydrous ethanol is added to gasoline, in the proportion of 20 to 25%, in order to increase the octane, improve the performance and reduce the pollution rates. However, for that use, ethanol must be practically free of water, with at least 99.6% of alcohol content (% in volume). The challenge is that the ethanol-water mixture presents an azeotrope, which hinders the separation in conventional methods, such as simple distillation. For the anhydrous ethanol production, extractive and azeotropic distillation are the methods most used, consisting on the addition of a third substance in the distillation column capable of changing the liquid-vapor equilibrium behavior of the system, modifying the relative volatility of the compounds of the initial mixture and thereby obtaining complete separation of the components. As an alternative to the various processes used, this work proposes the extractive distillation process using propylene glycol as the solvent, being the third component for the separation of the ethanol-water system. The choice of solvent is based on the miscibility with water and the ability to absorb it, as it has a low vapor pressure and, since it has been seen that many of the solvents already in use are toxic and are pollutants, such as ethylene glycol. Therefore, the ethanol separation process using propylene glycol as the solvent was evaluated using ProSimPlus software. It was simulated on the short-cut column, with the S/F ratios equal to 0.5, 0.7 and 0.9. The molar fraction of ethanol obtained in the distillate was higher than 0.994, which accounts for approximately 99.9% volume, and could thus be qualified as anhydrous ethanol. The obtained results showed that the azeotrope was broken, the distillation process was technically possible, applying the propylene glycol.

Keywords: Process simulation; Anhydrous ethanol; Azeotrope; Propylene glycol

Introduction

Anhydrous ethanol is of great importance in the industry, mainly in the fuel industry. According to the ANP (National Oil Agency) 20-25% of ethanol is permitted to be added to gasoline in order to increase its octane, improve the performance and reduce the pollution rates, as it decreases the emitted CO_2, reducing the emission of greenhouse gases and the energy dependence of fossil fuels. However, for the use of anhydrous alcohol with gasoline, it must be practically free of water (anhydrous), with a minimum of 99.6% alcohol content. According Gomis et al. [1], the water present in ethanol, from its production, causes the formation of two phases when mixed with gasoline in a certain proportion, resulting in engine problems.

The separation of the components of a mixture is of paramount importance in the chemical industry, distillation being the most used separation method, based on the difference in volatility of the components of a liquid mixture [2]. However, some mixtures have characteristics that prevent the total separation of their components, which makes it impossible to use the conventional distillation method.

When a boiling liquid produces a vapor of the same composition and, consequently, the liquid when it evaporates does not alter this composition and occurs the formation of azeotrope, in which the boiling point remains constant, the composition of the vapor phase becomes equal to that of the liquid phase, not allowing its components to be separated by the simple distillation process [3]. The ethanol-water system, for example, forms an azeotrope in compositions close to 0.88, on a molar basis.

It is necessary to use other methods for the dehydration of ethanol, with these systems, such as azeotropic or extractive distillation, consisting of the addition of a third substance in the distillation column, capable of altering the behavior of the liquid-vapor equilibrium in the system and obtaining total separation of its components. What differs from the azeotropic distillation to the extractive distillation is the volatility of the solvent added to the distillation column, where in azeotropic distillation there is the formation of a new azeotrope in the system, which does not occur in the extractive process, making its use more favorable.

The choice of the dehydrating agent should be made in a way that minimizes production costs, has low vapor pressure, has a greater affinity with water so as to entrain as little alcohol and as much water as possible and provide the desired separation using the minimum amount of solvent. Lee [4] reported that the addition of glycols as solvents breaks the ethanol-water azeotrope and changes the liquid-vapor equilibrium curve positively for ethanol dehydration. Ethylene glycol is the most commonly used solvent for the dehydration of ethanol by the extractive distillation method, however it is a slightly toxic compound. For this reason, the search for new solvents that are not harmful to health and the environment has increased.

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An important step in the process is the prior characterization of the mixture to be separated. ProSimPlus software is engineering software that performs mass and energy balances for a wide range of industrial processing plants. ProSimPlus solutions are used in the design and operation of existing plants to optimize performance, solve unit problems or maximize the efficiency of industrial plants by providing more than 70 unit operations [5].

On this, the present work aims to study and establish the operational conditions for the extractive distillation of ethanol using propylene glycol as the solvent, through ProSimPlus software. The choice of propylene glycol was performed because it met the requirements of a good solvent and due to the absence of information from it for the breakdown of the ethanol-water azeotrope.

Methodology

Process simulation

The thermodynamic model of ethanol - water - propylene glycol system was made by ProSimPlus software. Raoult's law modified with γ-Φ approach was used to represent the liquid-vapor equilibrium of the system. The activity coefficient (γ) was used in order to consider the non-ideal liquid phase. The vapor phase was considered ideal due to the process occurring at atmospheric pressure [6], then, Φ=1. Thus, the equation 1 can be written. The NRTL thermodynamic model was used to calculate the activity coefficient, since it corresponds to the results obtained by Meirelles et al. [7].

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

The thermodynamic model was validated by calculating the liquid-vapor equilibrium in the ProsimPlus simulator. Figures 1 and 2 show the liquid-vapor equilibrium diagrams generated by the ProsimPlus simulator for the ethanol-propylene glycol and water-propylene glycol systems, proving that there is no formation of azeotropes between them, making possible the study of propylene glycol as extractive agent of the ethanol-water system.

Figure 3 shows the liquid-vapor equilibrium curve (101.3 kPa) for the ethanol-water system, generated by the simulator, using the NRTL model.

A pseudo-binary diagram was constructed on a solvent-free basis with the liquid-vapor equilibrium data of the ethanol-water-propylene glycol ternary system. According to NEVES [8], the presence of the solvent in the vapor phase indicates that it is off the mass transfer process. This means solvent do not transfer itself, influencing the process only by its effect on the phase equilibrium. Then, the ternary system can be reduced to the ethanol-water binary system, according to equations 2 and 3:

$$x' = \frac{x1}{x1 + x2} = \frac{x1}{1 - x3} \qquad (2)$$

$$y' = \frac{y1}{y1 + y2} = \frac{y1}{1 - y3} \qquad (3)$$

x' and y' being the solvent free basis compositions, x_1, x_2 and x_3 the fractions in the liquid phase of ethanol, water and propylene glycol, respectively, and e y_1, y_2 e y_3 the fractions in the vapor phase of ethanol, water and propylene glycol.

Based on the work of Furter, liquid separating agents are generally present between 50 and 90% by weight of the liquid phase. The S/F (propylene glycol/feed) ratio was varied from 0.5; 0.7 and 0.9 by weight for the simulation of the ethanol-water-propylene glycol extraction 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 (N_F) and operating limit conditions: minimum reflux ratio (R_{min}) and minimum number of stages (N_{min}) (PROSIMPLUS, 2017). Figure 4 shows an illustrative schematic of the simulated process presented by the simulator.

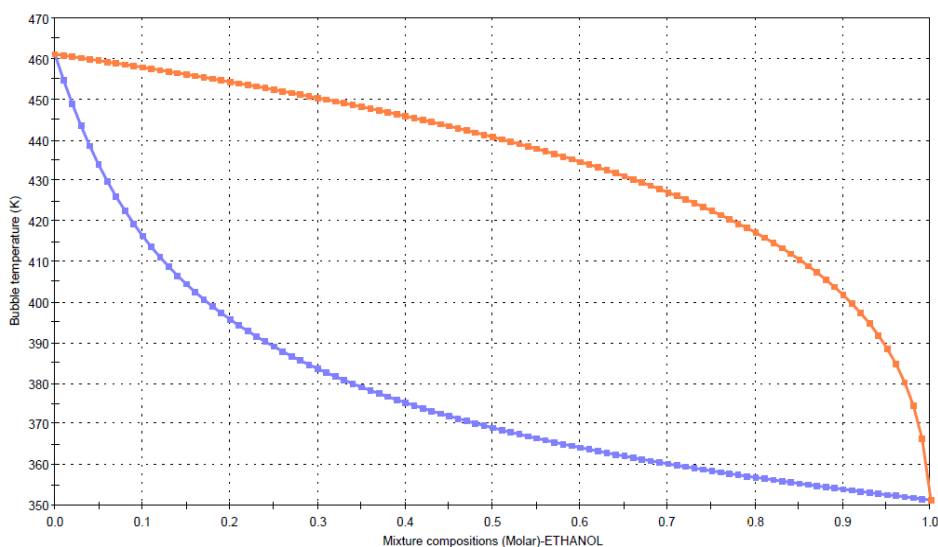To calculation of the minimum number of theoretical stages,

Figure 1: Liquid-vapor equilibrium of the ethanol-propylene glycol system.
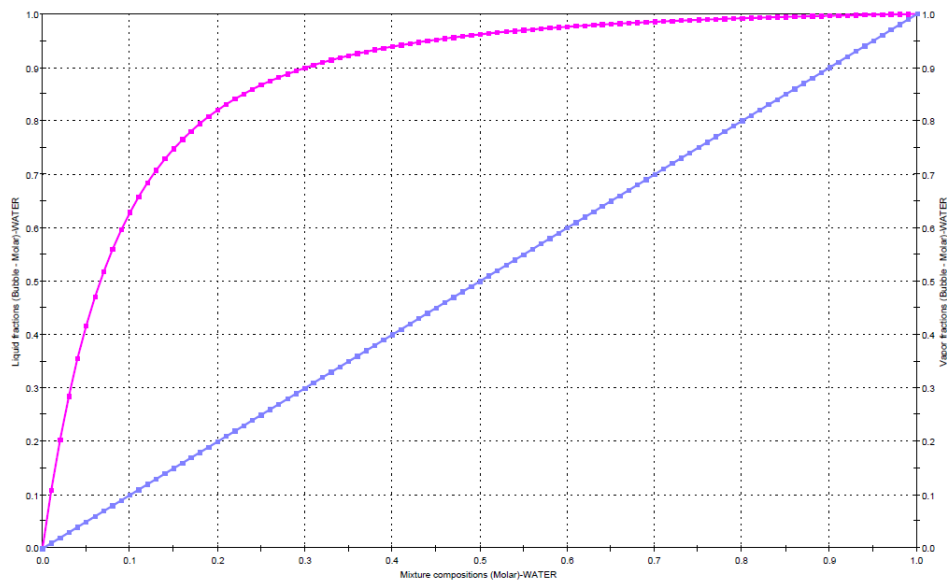
Figure 2: Liquid-vapor equilibrium of the water-propylene glycol system.
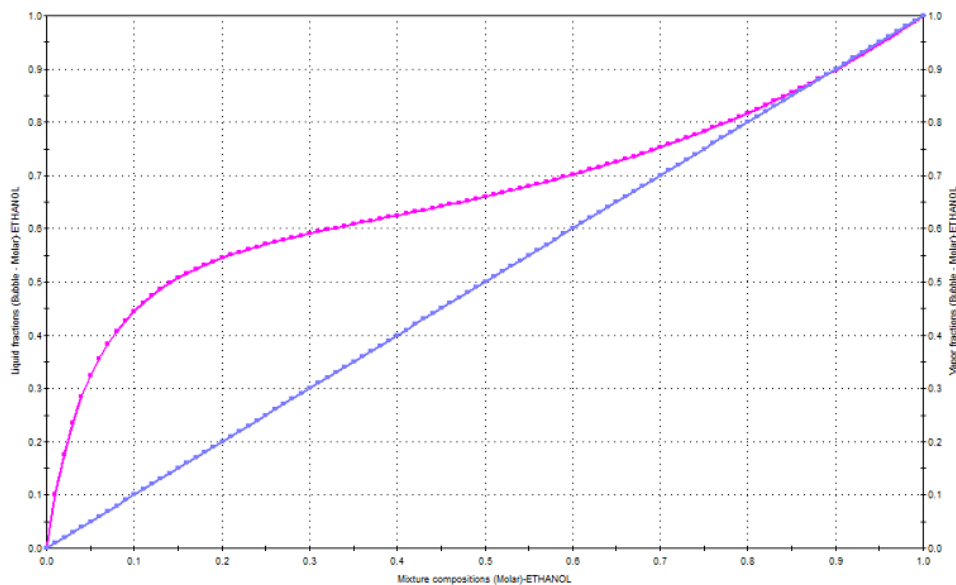

Figure 3: Liquid-vapor equilibrium of the ethanol-water system.

the FUG method uses the Fenske equation for the distillation of multicomponent systems, expressed in equation 4.

$$N_{min} = \frac{\ln \dfrac{x_{D,LK} x_{B,HK}}{x_{B,LK} x_{D,HK}} - 1}{\ln \alpha_{LK,HK}} \quad (4)$$

being LK the light component (more volatile compound of the system) and HK the heavy component, x_B and x_D the compositions of the liquid phase of the residue and distillate, respectively. The value of α is given by equation 5.

$$\alpha_{LK,HK}(T) = \frac{K_{LK}(T)}{K_{HK}(T)} \quad (5)$$

The number of ideal stages is determined by the Gilliland correlation, indicated in equation 6.

$$\frac{N - N_{min}}{N - 1} = f \frac{R - R_{min}}{R + 1} \quad (6)$$

The analysis of the minimum reflux ratio is given by the Underwood equation. It is necessary to find the value of A that satisfies equation 7.
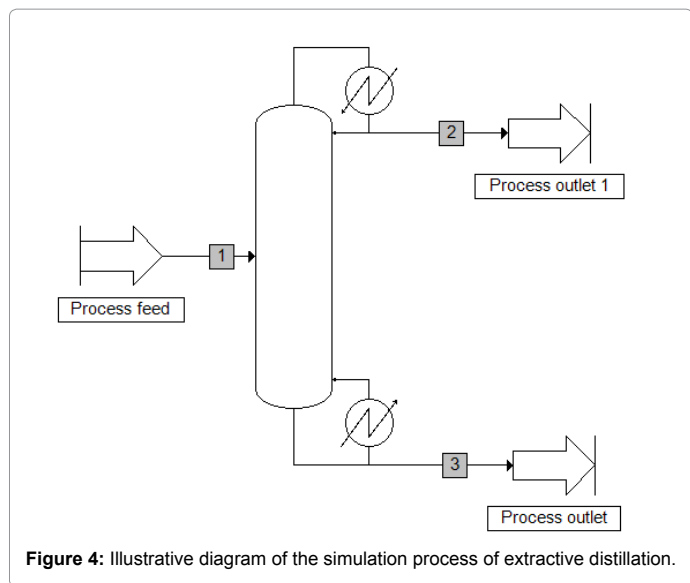
Figure 4: Illustrative diagram of the simulation process of extractive distillation.

Figure 5: Liquid-vapor equilibrium pseudo-binary for the ethanol-water-propylene glycol system.

Once the value of A is obtained, the minimum reflux ratio, expressed in equation 8, can be calculated.

$$(1-q)=\sum \frac{\alpha HKxF}{\alpha HK-A} \tag{7}$$

$$R_{min}=\frac{V}{D}=\sum \frac{\alpha HKxD}{\alpha HK-A} \tag{8}$$

Results

Figure 5 shows the pseudo-binary diagram for the ethanol-water-propylene glycol system. It is possible to observe the influence of the propylene glycol solvent on the liquid-vapor equilibrium, altering the volatility of the system and allowing the breaking of the azeotrope formed in the ethanol-water system, providing a greater dehydration of the ethanol. Thus, the use of propylene glycol in extractive distillation becomes favorable for the production of anhydrous ethanol.

The operational criteria considered efficient were based on the composition of the distillate in the extraction column, which should be 99.6% volume of ethanol. From the results obtained, the fraction of the distillate can be converted in % volume, where it reaches approximately 99.9% ethanol by volume. Table 1 presents the simulation data for the different S/F ratios.

Tables 2-4 show the effect of each S/F ratio, the minimum reflux ratio, the number of theoretical stages and the energy consumption on the molar composition of the distillate in the extraction column. The best operating condition is given by the simulator, with R/R$_{min}$ equal to 1.3. It is possible to observe that, as the S/F ratio increases, there is an increase in energy expenditure, which makes it more favorable to use S/F equal to 0.5, since for the three reasons there was efficiency in the fraction obtained in the distillate of the extraction column.

Due to lack of data in the library using propylene glycol as solvent breaking the azeotrope in the system of ethanol-water, Table 5 presents obtained results from this research just as presents results obtained by Silva et al. [9], this last one analyze azeotrope breaking in the system of ethanol-water using glycerol as third component to extractive distillation with distinct ratios of solvent/load. The ethanol molar fraction at vapor phase is showed like: y ethanol. Silva et al. reported
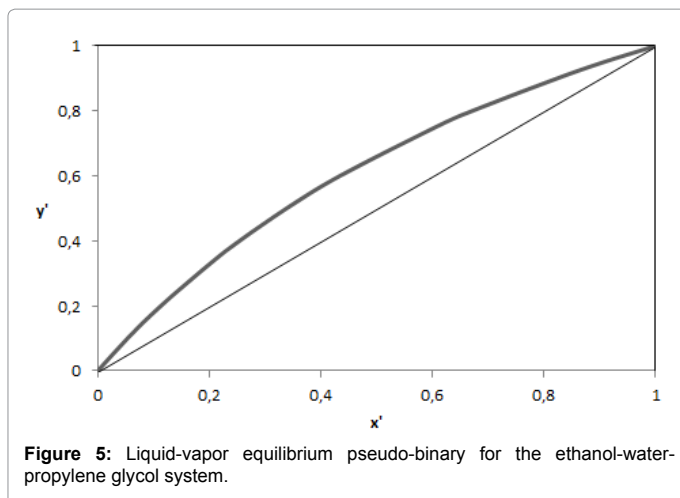
S/F=0.5		
Components	**Mass fraction (distillate)**	**Molar fraction (distillate)**
Ethanol	0.998	0.994
Water	0.002	0.006
Propylene Glycol	0	0
S/F=0.7		
Components	**Mass fraction (distillate)**	**Molar fraction (distillate)**
Ethanol	0.998	0.994
Water	0.002	0.006
Propylene Glycol	0	0
S/F=0.9		
Components	**Mass fraction (distillate)**	**Molar fraction (distillate)**
Ethanol	0.998	0.994
Water	0.002	0.006
Propylene Glycol	0	0

Table 1: Results of the simulation process of distillation of the ethanol-water-propylene glycol system.

R/R$_{min}$	Reflux Ratio	Number of theoretical stages	Condenser Duty (Kcal/h)	Reboiler Duty (Kcal/h)
1.05	2.021	47	242243	309583
1.1	2.117	42	251095	317336
1.2	2.310	36	266599	332840
1.3	**2.502**	**32**	**282104**	**348345**
1.4	2.695	30	297609	363849
1.5	2.887	29	313113	379354
1.7	3.272	26	344122	410363
2.0	3.850	24	390636	456877
3.0	5.775	21	545682	611922

Table 2: Operating conditions for S/F=0.5.

R/R$_{min}$	Reflux Ratio	Number of theoretical stages	Condenser Duty (Kcal/h)	Reboiler Duty (Kcal/h)
1.05	2.830	60	308459	446052
1.1	2.964	53	319312	456905
1.2	3.234	45	341019	478612
1.3	**3.503**	**41**	**362725**	**500318**
1.4	3.773	38	384431	522024
1.5	4.042	36	406137	543730
1.7	4.581	33	449549	587142
2.0	5.390	31	514668	652261
3.0	8.085	27	731729	869322

Table 3: Operating conditions for S/F=0.7.

R/R$_{min}$	Reflux Ratio	Number of theoretical stages	Condenser Duty (Kcal/h)	Reboiler Duty (Kcal/h)
1.05	3.808	82	387268	943925
1.1	3.989	72	401874	958531
1.2	4.352	61	431085	987743
1.3	**4.715**	**55**	**460297**	**1.02E+06**
1.4	5.077	52	489509	1.05E+10
1.5	5.440	49	518721	1.08E+10
1.7	6.166	45	577144	1.13E+10
2.0	7.254	42	664779	1.22E+10
3.0	10.88	37	956897	1.51E+10

Table 4: Operating conditions for S/F=0.9.

	Results obtained in this work	Results obtained by Silva et al.
S/F	y ethanol	y ethanol
0.5	0.994	0.9945
0.7	0.994	0.926
0.9	0.994	0.9986

Table 5: Comparative data of the molar fraction of ethanol in the vapor phase.

that the results obtained showed that the azeotrope between ethanol and water can be broken by glycerol using the solvent/ feed ratios used in its work. The molar fraction of ethanol in the vapor phase varied in the different S / F ratios, which did not occur in the results obtained in this work. It is possible to observe that, like glycerol, propylene glycol is also effective, positively influencing the liquid-vapor equilibrium curve of the ethanol-water system, making it possible eliminate the azeotrope.

Conclusion

The simulation study made it possible to establish previous operational conditions for an extractive distillation process to eliminate the ethanol-water azeotrope with propylene glycol as solvent. The use of software to characterize the mixture to be separated is of paramount importance in the industry, allowing predicting and improving the process.

The use of propylene glycol as the third component of extractive distillation is technically possible, breaking the azeotrope formed in the ethanol-water mixture and allowing the greater dehydration of the ethanol.

The solvent (propylene glycol) / feed (S/F) ratio did not interfere in the results, obtaining the same fraction of ethanol in the three ratios, being more viable the use of S/F=0.5, due to lower solvent expense and for achieving the composition of the distillate with lower energy consumption.

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