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SIMULATION OF THE EXTRACTIVE DISTILLATION OF ETHANOL-WATER SYSTEM: EVALUATION OF THE INFLUENCE OF DIFFERENT SOLVENTS

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Abstract. Distillation is one of the most important separation processes used in the chemical and petrochemical industry. The advent of computing has enabled the use of rigorous models for modelling complex distillation systems. Ethanol was chosen as product of interest because it is a clean-burning fuel, with the potential to reduce greenhouse gas emissions, and Brazil is the second producer of the world. Thus, this study used the software SuperPro Designer@ to simulate the separation of ethanol-water system. Firstly, it was done in a flash isothermal drum and, then using an extractive column operating in a continuous mode using glycerol, NaCl and $CaCl_2$ as separation agents, and the NRTL thermodynamic model to describe the vapor-liquid equilibrium (VLE). Data obtained after the simulation were compared with experimental data already published in literature, with good results. The maximum relative deviations in temperature were 0.10, 1.59, 2.55 and 2.44%; while the deviations for the composition of the distilled ethanol were 1.70, 3.52, 1.18 and 1.62% for the ethanol-water, ethanol-water-glycerol, ethanol-water-NaCl and ethanol-water-$CaCl_2$ systems, respectively. In all systems, it was possible to observe the positive behaviour of the NRTL model as well as the influence of the solvent in the VLE ethanol-water system.

Keywords: *inorganic salts, glycerol, azeotrope, extractive distillation.*

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1. Introduction

The use of fossil fuels and its damage to the environment is a global concern. Thus, biofuels, biodiesel and ethanol are a promising alternative to fossil fuel since they are clean-burn fuels (Gepros, 2012).

Currently, the fermentation process is responsible for most of the ethanol produced by industries; however, the solution of water-ethanol obtained after the simple distillation process has a molar concentration equal to 0.88 (azeotropic point). At this concentration, the separation of the two components by simple distillation at atmospheric pressure is impossible. Hence, in order to obtain anhydrous ethanol is necessary to use an entrainer that is able to change the VLE of ethanol-water system. This dehydration method can be done by two different types of distillation, azeotropic or extractive, in which a solvent is added, such as glycerol, ethylene glycol, benzene, pentane, furfural, diethylether, toluene, ionic liquids, and salts that change the VLE of ethanol-water system. The result is a distillate with a minimum content of 99.95 ºGL, thus fitting the right parameter to be mixed to gasoline.

Among the solvents able to change the VLE of ethanol-water mixture, one of the biodiesel’s production by-products will be addressed in this study - glycerol. The growth of demand and production of biodiesel motivated the choice of glycerol as the solvent of the extractive distillation process, because an increase in the production of this fuel will thereby increase the availability of glycerine in the market, which is currently most used as a raw material to the production of soaps. However, the soap industry will not be able to absorb such a large volume of raw materials, so it is extremely important to conduct researches in order to find possible alternative uses for glycerol.

Some salts when dissolved in a liquid mixture are able to change the VLE of the system if they are capable of performing a selective molecular association with one of the components present in the liquid phase (Schmitt & Vogelpohl, 1983). Based on the phenomenon of displacement of the azeotrope point, this paper will also study the saline extractive distillation using NaCl and $CaCl_2$ to change the VLE of ethanol-water mixtures. The goal is a possible reduction in the production cost, as the salt does not vaporises in the distillation process, the energy consumption is reduced, and the use of a solvent recovery column is not required.

In order to simulate all those processes listed above, this study uses a rigorous calculation model mass-energy-summation-enthalpy (MESH) present in the "software" SuperPro Designer v9.0, which mathematically models a distillation column, an isothermal flash drum and extractive distillation. The thermodynamic model non-random two liquids (NRTL) was used to predict the vapor-liquid equilibrium of all the systems tested in this work.

2. Literature review

Anhydrous ethanol obtained via extractive distillation has generated many publications, focusing on the design, optimization, and energy integration process.

The complete process of extractive distillation involves an extraction column and a solvent recovery column. Figure 1 illustrates a common flowsheet of the extractive distillation process.

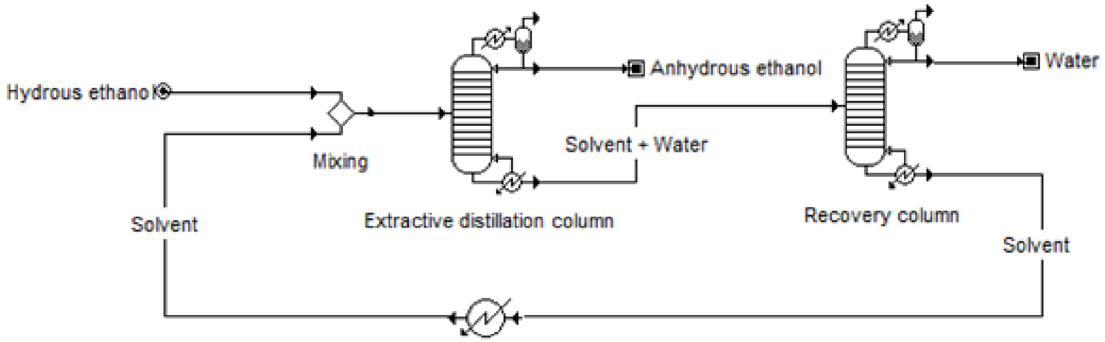

Figure 1. Usual configuration of an extractive distillation process

2.1. Influence of glycerol in the vapour-liquid equilibrium of the water-ethanol system

Over the years, many organic and toxic solvents had been used to improve the separation of ethanol-water system. Nowadays, the most used is ethylene glycol, a less aggressive solvent (Souza *et al.*, 2013). Nevertheless, in recent researches, the by product of the biodiesel process, glycerine, has been studied as an alternative solvent. Its use is so important, due to the fact that it can be recovered, and reused as a solvent in the ethanol production process (Apolinário *et al.*, 2012).

Figure 2 shows the comparison between the experimental data measured by Lee and Pahl (1985), Souza et al. (2013) and presented in DECHEMA (1981) for the binary system. Lee and Pahl (1985) studied the effect of eleven solvents in water-ethanol system, using an ebuliometer similar to an Othmer type, concluding that among all solvents containing glycols, glycerol was the best for the ethanol dehydration. This occurred because glycerol better interacts with water, promoting the elimination of the azeotrope, having the best effect on the vapour-liquid equilibrium.

Souza et al. (2013) and Souza (2012) studied the dehydration of ethanol measuring experimental data of an extractive distillation process using glycerol as an entrainer, analysing the influence of the amount of glycerine in the purity of the ethanol obtained. Solutions of ethanol-water were used with the molar fractions of 0.2, 0.4, 0.6 and 0.85 in ethanol and the amount of glycerine used was 0.5, 0.7 and 0.9 measured by weight. The results showed that the use of glycerol enhanced the ethanol concentration on the top of the column. The azeotrope was ‘broken’ only when the ethanol concentration in the feed was 0.85, for every concentration of solvent tested.

The nomenclature S/F was used to indicate the amount of glycerine used in each test as defined by Equation 1.

$$\mathbf{S/F} = \frac{\mathbf{mass}_{(\mathbf{glycerol})}}{\mathbf{mass}_{(\mathbf{etOH+\ H_2O})}} \tag{1}$$

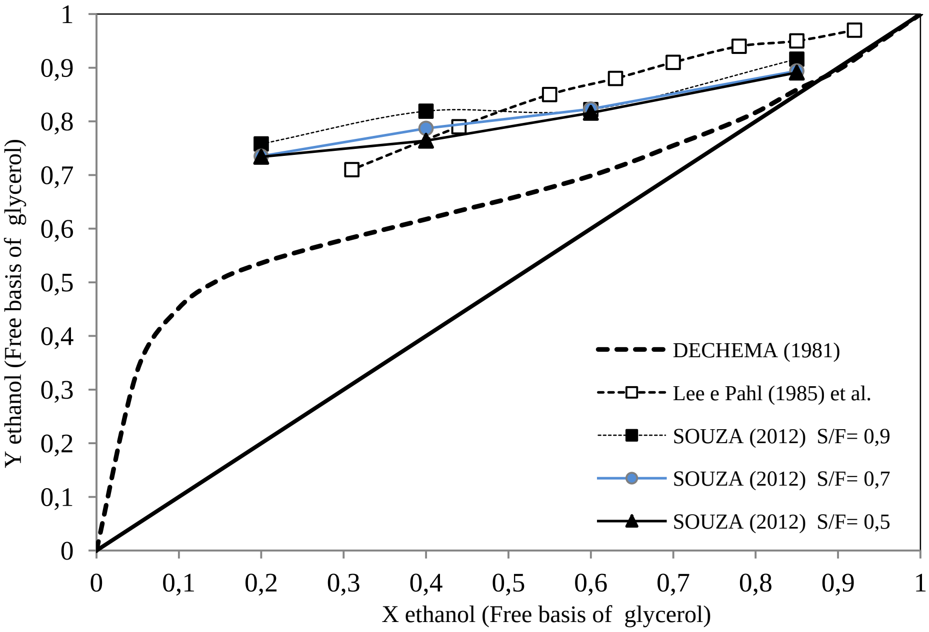

Figure 2. Effect of glycerol on vapour-liquid equilibrium of ethanol-water system (Souza *et al.*, 2013; Souza, 2012; Lee & Pahl, 1985; DECHEMA, 1981)

Contreras et al. (2014) performed experimentally the extractive distillation of ethanol-water system using glycerol as solvent, and simulated the same process using the thermodynamic model NRTL, and the software Aspen Plus. In both procedures, an ethanol-water mixture with the concentration of 94% (w), with different values of S/F were fed into the column. The result of the simulation and the experimental procedure was a distillate with a concentration exceeding 98% (w), with the exception of simulation done for S/F equal to 0.5, when the distillate obtained had a mass concentration slightly more than 96%. The results demonstrated the efficacy of glycerol in eliminating the azeotrope, coupled with the fact that glycerol has a low cost.

2.2. Influence of salt effect on the vapour-liquid equilibrium of water-ethanol system

The study of the influence of salts on the vapour-liquid equilibrium began in the thirteenth century, with the use of potassium carbonate on the distillation process of an alcoholic fermented liquid to enrich the steam. However, only in the nineteenth century, some authors studied the influence of dissolved salts in the liquid phase, from VLE data of ethanol-water mixture (Furter, 1972).

Furter and Cook (1967) and Furter (1977) conducted researches in order to find empirically thermodynamic parameters to report the influence of salts in the vapour-liquid equilibrium of water-ethanol system. Most of the salts tested by them were more soluble in water than in ethanol, favouring the enrichment of the vapour phase with the desired product. Among all salts tested, potassium acetate and calcium chloride have shown better results. However, salts such as mercuric chloride, cupric chloride, calcium acetate, and barium acetate have shown an inverse pattern, showing a preference for the solubilisation in ethanol. Thus, the choice of salt has a fundamental importance in ensuring the success of saline extractive distillation, as well as the operational difficulties, corrosion and incrustation of equipment, defaulting the handling and storage and melting temperature (Soares *et al*. 2015; Soares, 2010).

According to Schmitt and Vogelpohl (1983), a salt is capable to alter the composition of the vapour-liquid equilibrium because it is capable to perform a selective molecular association with one of the components of the liquid phase. This phenomenon can change the relative volatility displacing or even eliminating the azeotrope, allowing a more efficient separation. This tendency of enrichment the vapour phase with the component that the salt used is less soluble in the liquid phase, is called "salt effect on the vapour-liquid equilibrium" (Long & McDevit, 1952).

During the period between 1930 and 1950, many plants used the saline extractive distillation process called HIAG (Holz Industrie Actien Geselleschaft), which a mixture of potassium and calcium acetate were introduced in the column on the top reflux stream. This technology used to be present in a total of 100 plants in Europe with a total installed capacity of 43,000 tons per hour. In Brazil, the last plant using this technology stopped operation in 1945 (Frolkova & Raeva, 2010). As mentioned above, the use of salts as separating agents in the extractive distillation is not a new technology, however, in contrary to conventional solvents, salts are non-toxic, and do not vaporize in the distillation process, reducing energy consumption (Soares *et al*., 2015; Soares, 2010). Because of the current national economy and energy situation, the resumption of researches to correct pre-existing technical problems in the original process is justified.

Soares et al. (2015) and Soares (2010) studied the separation of ethanol-water mixture in the presence of sodium chloride, calcium chloride, sodium acetate, potassium acetate and calcium nitrate. It was concluded that all the salts used were able to change the VLE, and hence it was possible to produce a distillate with ethanol concentration above the azeotropic point as shown in Figure 3.

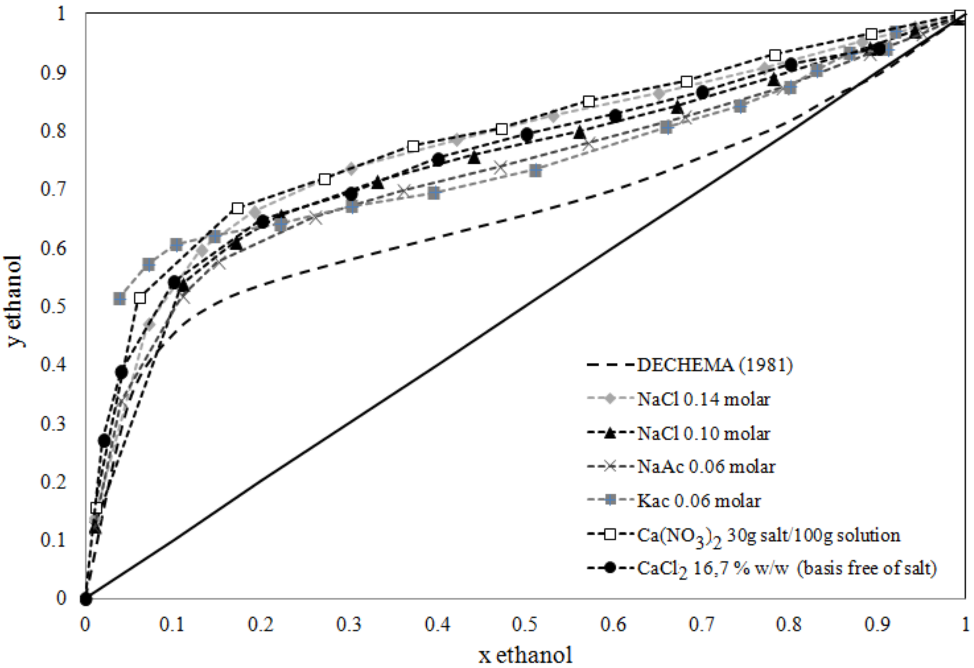

Figure 3. Experimental and predicted liquid–vapour equilibrium curves for water–ethanol system with different concentrations of salts (DECHEMA, 1981; Soares *et al.*, 2015; Soares, 2010)

2.3. Simulation

The simulation of the distillation column was studied using a rigorous calculation model known as mass-energy-summation-enthalpy (MESH) (Henley & Seader, 1981). Following the methodology proposed by Naphtali and Sandholm (Henley & Seader, 1981), the equations were solved at the same time, obtained from the balance sheet (mass and energy), and the equilibrium relationships. A more detailed and thorough approach to Naphtali-Sandholm method is presented in Kister (1992), and Henley and Seader (1981).

2.4. Thermodynamic model

The behavior of the systems involving water-ethanol equilibrium data can be well represented considering an ideal vapour phase, and a non-ideal liquid phase. Equation 2 describes the equilibrium of the system under those conditions (Prausnitz *et al*., 2000).

$$y_i P = \gamma_i x_i P_i^{sat} \tag{2}$$

with P^{sat} as the saturation pressure (Pa), P the absolute pressure (Pa) and x_i and y_i are the molar fractions of the liquid and vapour phases, respectively and γ_i is the activity coefficient.

The non-random two liquids (NRTL) model was chosen to predict the non-ideal liquid phase because it can represent multi-component mixtures containing alcohols.

The parameters showed in Table 1 were obtained by Voutsas et al. (2011) for the ethanol-water binary mixture, and used to calculate the right value to be inserted in the NRTL model by using the equation 3. However, the parameters corresponding to the pairs glycerol-ethanol and water-glycerol used were obtained by Coelho et al. (2011), and they are shown in Table 2. The constant α, present in the NRTL model, was considered equal to 0.3.

$$\frac{\Delta g_{ij}}{R} = a + b.T + c.T^2 \quad (3)$$

As the NRTL model does not describe the thermodynamic equilibrium of salts, the parameters corresponding to them had been considered zero. As a result, the salt altered the equilibrium vapour-liquid of ethanol-water system even without any participation in the calculations performed with the model.

Table 1. NRTL parameters used to describe ethanol (1)-water (2) system (Voutsas *et al.*, 2011)

Parameter	a	b	c
$\frac{\Delta g_{12}}{R}$	-508,37	3,391	-0,00584
$\frac{\Delta g_{21}}{R}$	-763,53	5,1484	-0,00332

Table 2. NRTL parameters obtained by Coelho et al. (2011) of the binary systems, water-glycerol e ethanol-glycerol

System	$\frac{\Delta g_{12}}{R}$	$\frac{\Delta g_{21}}{R}$
water (1) - glycerol (2)	-595,94	253,74
ethanol (1) - glycerol (2)	-198,84	697,02

3. Materials and methods

3.1. Materials

This study used the software SuperPro Designer v9.0 to simulate two processes: i) the separation of an ethanol-water mixture in flash drums, and ii) an extractive distillation column fed with ethanol-water, ethanol-water-glycerol, ethanol-water-NaCl and ethanol-water-$CaCl_2$ mixtures.

3.2. Methods

The procedure adopted for the simulations is explained in three different subtopics, according to the mixtures: ethanol-water, ethanol-water-glycerol, and ethanol-water-salt.

All the simulations were done considering normal pressure (1 atm), and the distillation columns operated in a continuous mode. So, the simulations were performed using the experiments published by Soares et al. (2015) and Souza et al. (2013), in order to ratify the behavior by the thermodynamic model, to analyze the effect of the different solvents in the ethanol-water separation to make a future scale-up of the process.

3.2.1. Ethanol-water system

An equimolar mixture was simulated in a flash, with different operational temperatures.

In addition, the same mixture was simulated in a distillation column, composed by a total condenser, a partial reboiler and 6 theoretical plates, operating with an efficiency of 80%. The mixture was fed in the third plate, operating under a top reflux ratio equal to 5, and the molar ratio between the bottoms product and the feed was equal to 0.6.

3.2.2. Ethanol-water-glycerol system

The experiments performed by Souza (2012) were simulated in this work. For this study, it was simulated an extractive distillation with a column composed of a total condenser and a partial reboiler, operating with an efficiency of 100%, fed by a molar concentration of ethanol from 0.2 to 0.85, and S/F values equal to 0.5, 0.7 and 0.9. The number of stages of equilibrium was defined as equal to 2 when the feeding concentrations were 0.2, 0.4 and 0.6, and equal to 1 for the composition of 0.85.

Souza et al. (2013), Soares (2010) and Soares et al. (2015) carried out their experiments using the same packed distillation column, present in the Applied Thermodynamics and Biofuel Laboratory in the Chemical Engineering Department at UFRRJ. This work used a column composed by plates, because that was the only option present in the software SuperPro Designer. However, all the simulation settings were defined in order to represent as much as possible the reality in the lab. Keeping the same aim, as the software does not allow the use of rigorous calculus in a batch mode, this paper used a very high value of top reflux rate, 10^7, in order to approximate the simulation conditions to the experimental procedure, when a column used by Souza (2012) and Soares (2010) operated in batch mode. In that case, once the steady state was achieved, vapor samples were collected, and their temperature and concentration were analyzed.

As described by Souza et al. (2013), the elimination of the azeotrope occurs in the bottom of the column, when the charge is equal to 0.85 molar in ethanol in the presence of glycerol. Thus, the ethanol concentration is the same throughout the packed section, independently of the number of stages. Souza et al. (2013) reported that the concentration of ethanol in the top and bottom are approximately the same, and the result was less than one stage of equilibrium, because the packed section is small. Therefore, for all the situations in which the molar concentrations of ethanol are equal to 0.85, the number of plates chosen to compose the columns is only one. This also described the system when salts are used as entrainers.

3.2.3. Ethanol-water-salt system

The simulation of the extractive distillation was based on the experiments carried out, and described by Soares (2010) and Soares et al. (2015). Although the experiments had analyzed the effect of five different salts, this work only studied systems containing two of them, NaCl and $CaCl_2$. The distillation column was fed by a mixture with molar compositions of ethanol (free basis of salt) equal to 0.02, 0.25, 0.4, 0.6 and 0.85. The number of plates were set equal to 2 when the molar ratio of ethanol in the feed composition was 0.02, 0.25, 0.4 and 0.6, and equal to 1 for the composition of 0.85. Because of the absence of VLE data in the literature describing the equilibrium of the ternary ethanol-water-NaCl, the same procedure was adopted in this study as well as was proposed by Farelo et al. (2004) and used by Soares et al. (2015). Empiric equations were used to calculate the saturation concentration, as is showed in equations 4, 5 and 6. For the system that used $CaCl_{2,}$ its concentration was equal to 16.7% w/w (free basis of salt) as investigated by Nishi (1975) and also used by Soares et al. (2015) and Soares (2010).

$$\mathbf{S = \frac{C\cdot(1-X)}{C+X} \cdot S_{water}} \tag{4}$$

$$\mathbf{C = 0{,}0956424 \cdot exp\,(0{,}0072512 \cdot T)} \tag{5}$$

$$S_{water} = 7{,}78461 - 0{,}01566 \cdot T + 0{,}000034 \cdot T^2 \qquad (6)$$

with S as the saturation of the salt in the alcohol mixture (mol/kg), T (K) the system temperature, X is the mass fraction of ethanol in the mixture, and S_{water} the solubility of the salt in pure water.

4. Results and discussion

This section presents the simulation results as well as the comparison with the experimental and predicted data found in the literature. The results are explained separately for the each system: ethanol-water, ethanol-water-glycerol and ethanol-water-salt.

4.1. Ethanol-water system

Prior to the simulation steps, the NRTL thermodynamic model was validated and applied to correlate the data. Therefore, the simulation results obtained were compared with the vapor-liquid equilibrium data acquired by DECHEMA (1981). This study uses relative deviation to compare all the simulated results with the experimental, as expressed in equation 7.

$$\mathbf{DR_i} = \frac{|\mathbf{exp-sim}|}{\mathbf{exp}} . \mathbf{100} \qquad (2)$$

with DR_i as the relative deviation of the variable i, 'sim' represents the results obtained in the simulation, and ‘exp’ the experimental data.

Flash drum

The concentration obtained in the top and bottom products for all flash drums simulated – and the comparison with the vapor-liquid equilibrium data acquired by Dechema (1981) – are presented in Figures 4 and 5. The results presented in Figures 4 and 5 are summarized in Table 3 with the standard deviations.

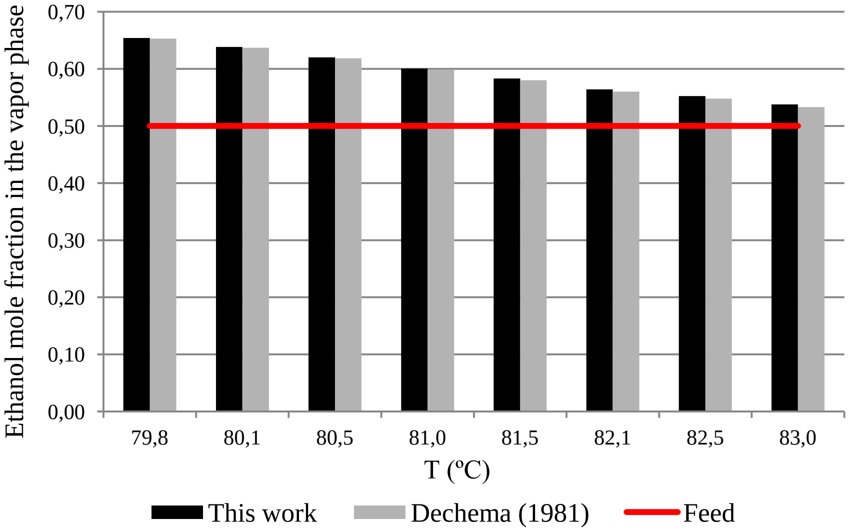

Figure 4. Simulated flash drums of ethanol–water system: comparison of vapor data simulated in this work and of ethanol–water system from DECHEMA (1981)

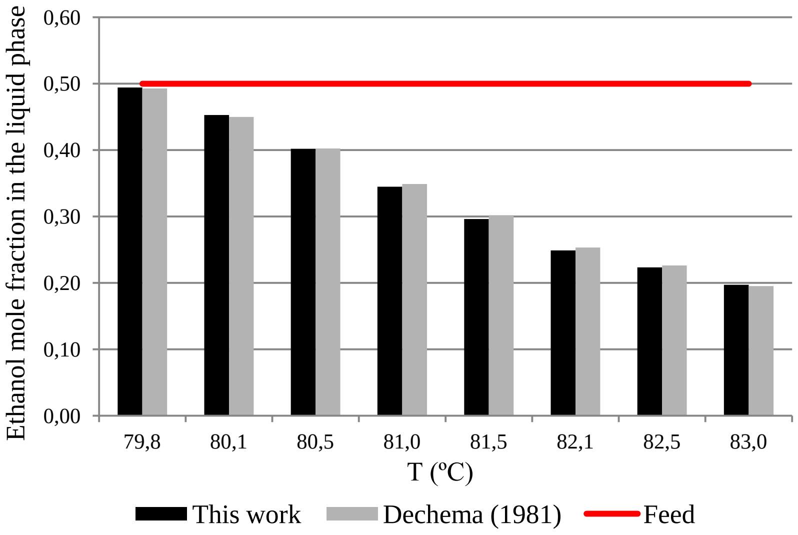

Figure 5. Simulated flash drums of ethanol–water system: comparison of vapor-liquid equilibrium data simulated in this work and of ethanol–water system from DECHEMA (1981)

Table 3. Comparison between VLE data obtained by Dechema (1981) and the data predicted in this work, using flash calculations

T (ºC)	$x_{ethanol}$ *	$x_{ethanol}$ This work	RDx (%)	$y_{ethanol}$ *	$y_{ethanol}$ This work	RDy (%)
79.8	0.49	0.49	0.29	0.65	0.65	0.16
80.1	0.45	0.45	0.64	0.64	0.64	0.22
80.5	0.40	0.40	0.14	0.62	0.62	0.28
81.0	0.35	0.34	1.20	0.60	0.60	0.39
81.5	0.30	0.30	1.88	0.58	0.58	0.54
82.1	0.25	0.25	1.69	0.56	0.56	0.71
82.5	0.23	0.22	1.26	0.55	0.55	0.78
83.0	0.20	0.20	0.89	0.53	0.54	0.89

*DECHEMA (1981)

The low deviation values for the flash simulation show that the NRTL thermodynamic model is able to predict the VLE of this mixture, thus completing the first stage of model validation.

Distillation

In order to validate the simulation of the distillation column, the data obtained were compared with the experimental result presented in Dechema (1981) for each plate simulated in the column.

The results of the simulation and the experimental equilibrium data (DECHEMA, 1981) are represented in Figures 6 and 7. Table 4 includes all the values, as well as the relative deviation resulting from the comparison between the two results.

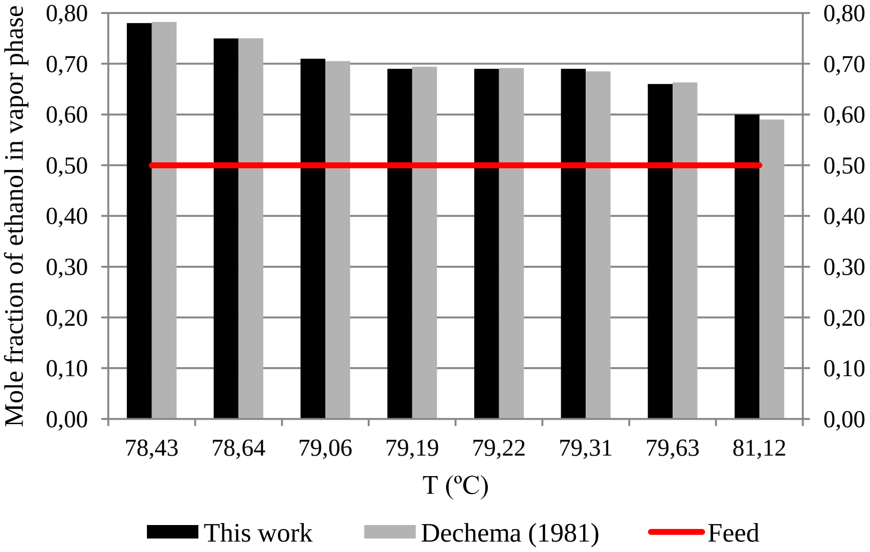

Figure 6. Simulation of the ethanol-water system separation: comparison of vapor concentration of ethanol and in the ethanol–water system from DECHEMA (1981).

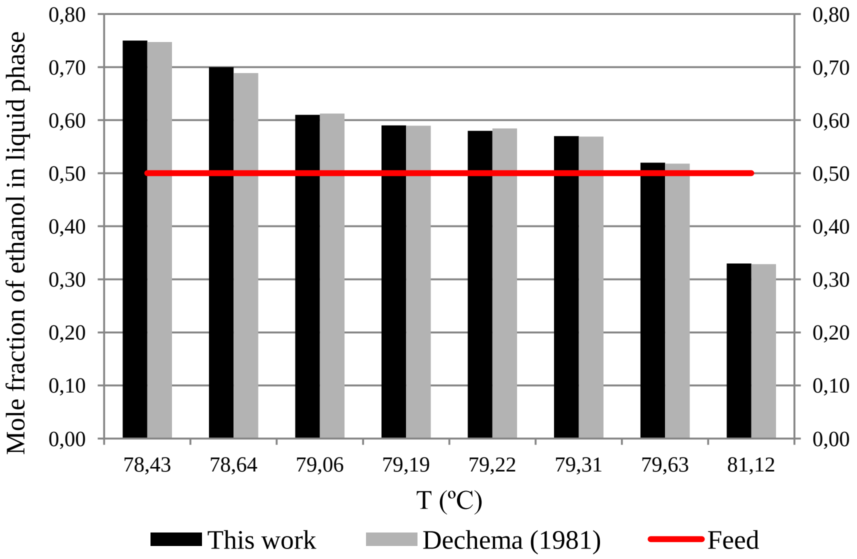

Figure 7. Simulation of the ethanol-water system separation: comparison of predicted liquid concentration of ethanol and in the ethanol–water system from DECHEMA (1981)

The results of all the deviations also show that the NRTL thermodynamic model is capable of describing the vapor-liquid equilibrium of ethanol-water system with good accuracy.

Table 4. Comparison between VLE data presented in Dechema (1981) and the simulated data predicted using a distillation column

T (ºC)	$x_{ethanol}$ *	$x_{ethanol}$ This work	DRx (%)	$y_{ethanol}$ *	$y_{ethanol}$ This work	RDy (%)
78.43	0.75	0.75	0.37	0.78	0.78	0.31
78.64	0.69	0.70	1.61	0.75	0.75	0.03
79.06	0.61	0.61	0.41	0.71	0.71	0.68
79.19	0.59	0.59	0.06	0.69	0.69	0.58
79.22	0.58	0.58	0.77	0.69	0.69	0.25
79.31	0.57	0.57	0.18	0.68	0.69	0.75
79.63	0.52	0.52	0.35	0.66	0.66	0.50
81.12	0.33	0.33	0.43	0.59	0.60	1.70

*DECHEMA (1981)

4.2. Ethanol-water-glycerol system

Figures 8 and 9 contain the results of the simulations, obtained varying the composition of ethanol from 0.2 to 0.85, as well as the experimental and modeling results obtained by Souza et al. (2013). The charge mole fractions were represented by X (free basis of glycerol), while the mole fractions of the distillate were represented by the letter Y (free basis of glycerol).

The experimental results simulated by Souza et al. (2013) were used to compare the simulated results obtained in this work, and the relative deviations between them are showed in Table 5.

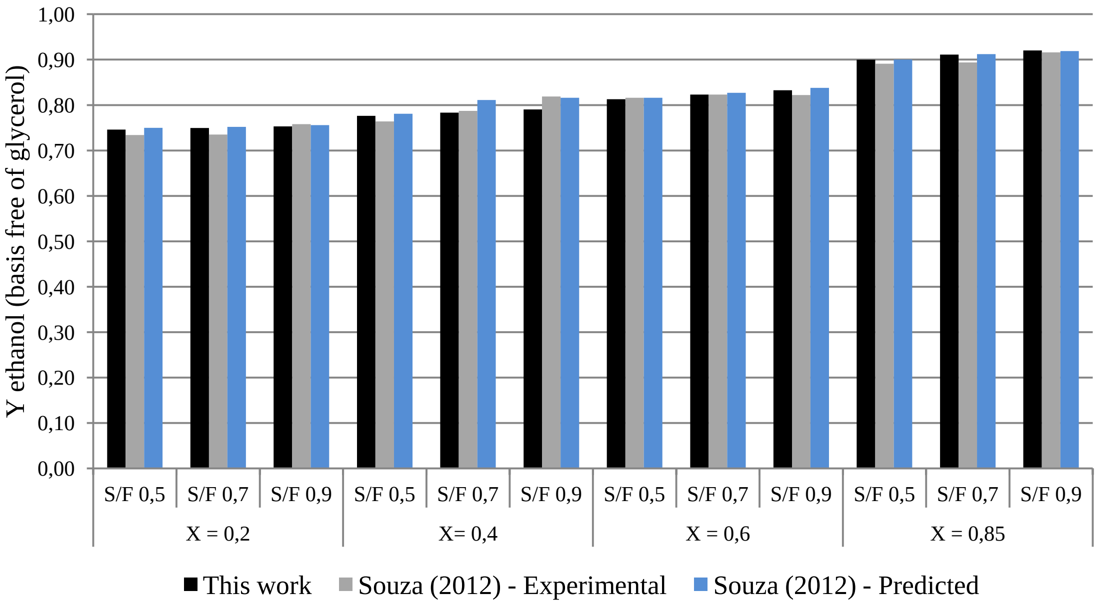

Figure 8. Comparison between the concentration of the distillate obtained in this work and the VLE predicted and measured by DECHEMA (1981)

The results of the simulations done in the software were compared with the experimental and also simulated results obtained by Souza et al. (2013) and Souza (2012). Because of that, it was calculated two deviations, one relative to experimental data and the other relative to the also simulated results. Table 5 shows all the results that explain that NRTL model is efficient in describing the vapor-liquid equilibrium of the ethanol-water-glycerol mixture, due to the low deviation reached.

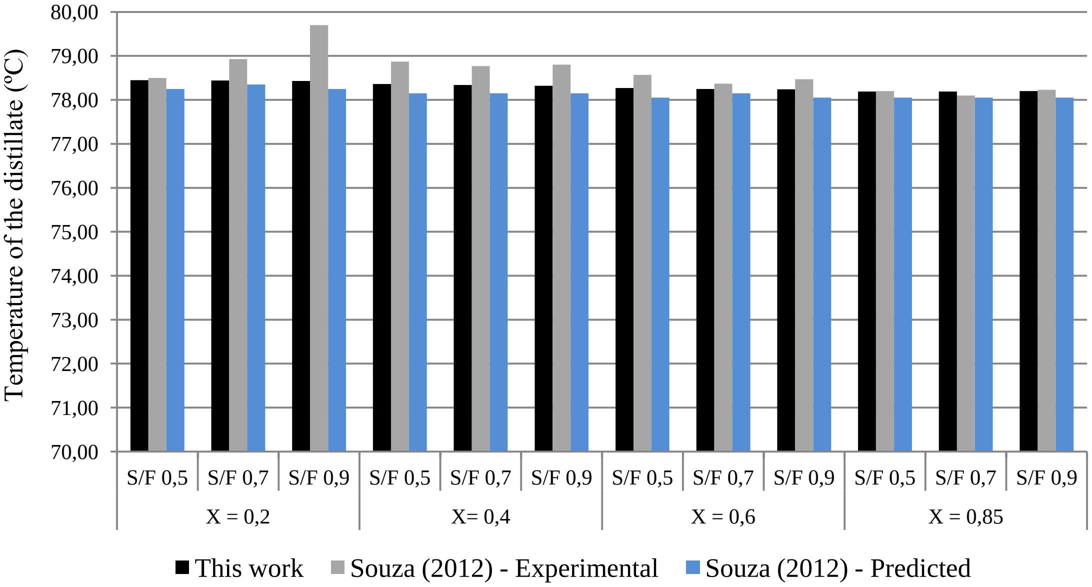

Figure 9. Comparison between the temperature of the distillate obtained in this work and the VLE predicted and measured by Souza et al. (2013) and Souza (2012)

Table 5. Comparison between the experimental and simulated results obtained by Souza (2012) and the data obtained in the simulation performed in this work

X	S/F	DR Y (experimental, %)	DR Y (simulated, %)	DR T (experimental, %)	DR T (simulated, %)
0.20	0.5	1.65	0.52	0.06	0.26
	0.7	1.99	0.31	0.62	0.11
	0.9	0.64	0.38	1.59	0.23
0.40	0.5	1.63	0.59	0.65	0.27
	0.7	0.45	3.40	0.55	0.24
	0.9	3.52	3.16	0.61	0.22
0.60	0.5	0.37	0.37	0.38	0.28
	0.7	0.00	0.48	0.15	0.13
	0.9	1.27	0.66	0.29	0.24
0.85	0.5	1.00	0.01	0.01	0.18
	0.7	1.91	0.10	0.12	0.18
	0.9	0.48	0.15	0.04	0.19

The highest deviation was 1.59 and 3.52% for temperature and mole fraction, respectively. However, in the experimental results reported by Souza et al. (2013), the elimination of the azeotrope was only evidenced when the feeding concentration of ethanol was equal to 0.85. This occurred for all S/F values used, because of the high quantity of glycerol, that causes a more significant effect changing the VLE of the ethanol-water system. Moreover, as reported by Souza et al. (2013) and confirmed in this paper, glycerol was not found in the distillate for any S/F value used.

Despite this, it is extremely important to emphasize that, for all molar concentrations of ethanol, independently on the S/F ratio applied, glycerol was effective in eliminating the VLE of the ethanol-water system, generating a richer distillate in ethanol.

4.3.Ethanol-water-salt systems

Figures 10 and 11 contain the results of the simulations using sodium chloride and calcium chloride as solvents, as well as the results obtained by Soares et al. (2015), which are all expressed in a free basis of salt.

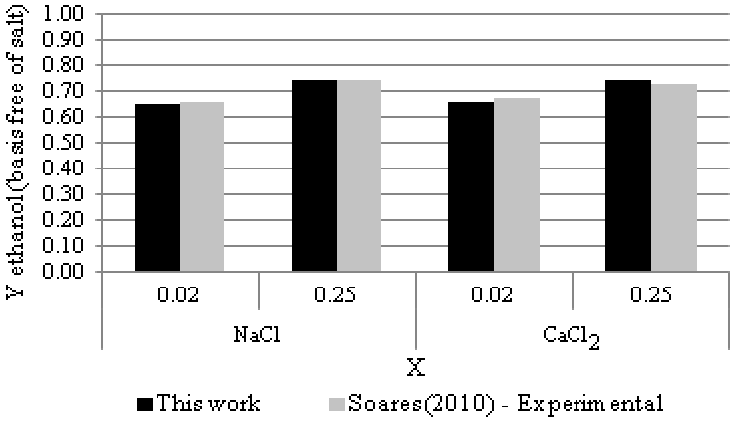

Figure 10. Comparison between the concentration of the distillate obtained in the simulation, and the VLE measured by Soares et al. (2015)

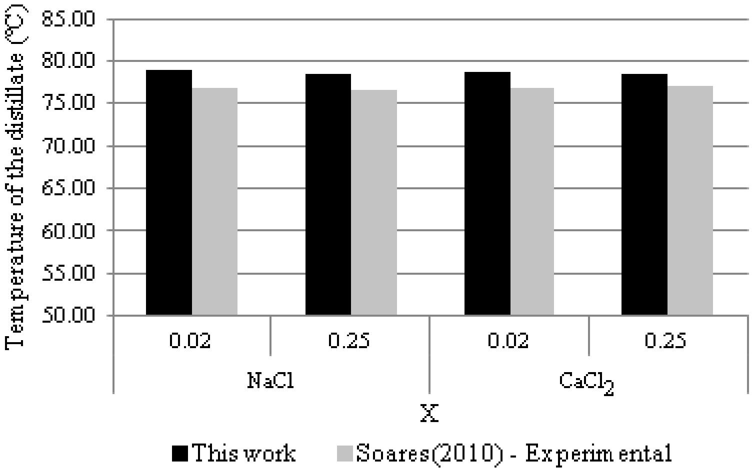

Figure 11. Comparison between the temperature of the distillate obtained in the simulation, and measured by Soares et al. (2015)

Soares et al. (2015) and Soares (2010) conducted the experiments using only two different solutions, with 7 and 52 GL grade or 0.02 and 0.25 mole fraction. However, in this work, it was simulated systems with additional concentrations, in order to study the behavior of the salts in solutions with different concentrations. The results and relative deviations are shown in Table 7.

Comparing the deviations shown in Table 7, it can be stated that the simulations conducted with the software matched very well the experiments performed by Soares (2010), with a maximum relative deviation in temperature and mole fraction equal to 2.55 and 1.62%, respectively. However, as observed by the experimental results reported by Soares et al. (2015), the elimination of the azeotrope was not observed.

Table 1. Comparison between the experimental results obtained by Soares et al. (2015), and the data predicted during the simulation performed

Salt	$x_{ethanol}$	$y_{ethanol}$ Literature	$y_{ethanol}$ This work	DR y (%)	T (°C) Literature	T (°C) This work	DR T (%)
NaCl	0.02	0.66	0.65	1.18	76.88	78.84	2.55
	0.25	0.74	0.74	0.04	76.62	78.47	2.41
	0.40	-	0.76	-	-	78.41	-
	0.60	-	0.79	-	-	78.32	-
	0.85	-	0.86	-	-	78.20	-
$CaCl_2$	0.02	0.67	0.66	1.30	76.92	78.80	2.44
	0.25	0.73	0.74	1.62	76.97	78.46	1.94
	0.40	-	0.76	-	-	78.41	-
	0.60	-	0.79	-	-	78.33	-
	0.85	-	0.87	-	-	78.20	-

The NRTL model was applied, for the simulations, considering the thermodynamic parameters for the salts equal to zero. According to Schmitt and Vogelpohl (1983), salts dissolved in a liquid mixture are able to change the vapor-liquid equilibrium, because they are capable to perform a selective molecular association with one of the components present in the liquid phase. Both salts used in this work dissolve better in water than in ethanol, promoting an increase in the relative volatility of ethanol (Soares, 2010; Soares *et al*., 2015; Leal *et al*., 2015; Jurado *et al.* 2015). Therefore, the salt used was able to influence the VLE of the ethanol-water system, even without participating in the mathematical modeling performed by the NRTL model. It is important to emphasize that this study proves that the influence of salts in the VLE of the ethanol-water system occurs at the base of the column, so it is not necessary to fed the salt at the top of the column, avoiding problems such as incrustation, and corrosion along the column.

5. Conclusions

The NRTL model describes quite well the vapor-liquid equilibrium of the water-ethanol system whether or not a separating agent is used. This study ratifies the effectiveness of all the separating agents used – glycerol, calcium chloride and sodium chloride – in changing the VLE of the ethanol-water mixture. As observed experimentally and confirmed by this study, it was possible to achieve in all simulations a richer distillate in ethanol. However, as in the experiments simulated, the elimination of the azeotrope was evidenced only when the molar concentration of ethanol fed in the column was equal to 0.85 (free basis of glycerol), for all the S/F values used. The use of a quaternary system composed of ethanol-water-glycerol-salt deserves special attention in further studies, since the use of the salt would reduce the demand for glycerol, and would lead to a reduction in energy consumption by the reboilers.

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