Simulation of liquid-liquid extraction to recover citric acid using 1-Butanol as solvent

Simulação da extração líquido-líquido para recuperar ácido cítrico usando 1-Butanol como solvente

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RESUMO
O ácido cítrico é um ácido orgânico fraco que pode ser encontrado nos cítrinos, com diversas aplicações industriais. O processo de separação por extração líquido-líquido pode ser usado para a recuperação do ácido cítrico, a partir de seu caldo de fermentação. O objetivo desse trabalho foi simular no software Aspen Plus o processo de recuperação do ácido cítrico usando como solvente o 1-butanol. Foram coletados da literatura dados experimentais de equilíbrio líquido-líquido para o sistema água + 1-butanol + ácido cítrico, nas temperaturas de 5,5 °C, 15 °C e 25 ºC, e posteriormente à aplicação das correlações de Othmer-Tobias e Hand foi possível assegurar a consistência termodinâmica desse conjunto de dados. O modelo termodinâmico NRTL foi utilizado, e seus parâmetros foram ajustados pelo código do TML. Com os resultados obtidos, pôde-se afirmar que houve recuperação do ácido cítrico, e a quantidade de solvente utilizado dependerá da concentração de ácido cítrico o qual é alimentado ao processo.

Palavras-chave: Equilíbrio líquido-líquido, consistência termodinâmica, ácido cítrico.

ABSTRACT
The citric acid is a weak organic acid that can be found in citrus, with several industrial applications. The aim of this paper was to simulate in the Aspen Plus the recuperation of citric acid using the 1-butanol as solvent. The experimental data of liquid-liquid equilibrium for the system water + 1-butanol + citric acid was collected under the 5,5 °C, 15 °C e 25 ºC temperatures from the literature. After Othmer-Tobias e Hand correlations appliance was possible to affirm the thermodynamic consistence of thhis data set. The NRTL thermodynamic model was used, and your parameters was adjusted with the TML code. The results points to recuperation of the citric acid, and the quantity of solvent used depends of the citric acid concentration that was alimented in the process.

Key words: Liquid-liquid equilibrium, thermodynamic consistency, citric acid.

1 INTRODUCTION
Citric acid, also known as hydrogen citrate, with its official name 2-hydroxy-1,2,3-propanotricarboxylic acid, is a weak organic acid that can be found in citrus fruits. The acidity of citric acid is due to the three carboxyl groups -COOH that can lose a proton in solutions. Therefore, a citrate ion is formed. Citrates are good pH controllers for acidic solutions (FIB, 2014).

Citric acid can be used to provide a pleasant and sour taste to food and drinks. It can also be applied in additive detergents, pharmaceuticals, cosmetics, and personal care products (Soccol et al., 2006).

The manufacture of citric acid can be performed through three processes: Koji, in which substrate is solid, using a specific strain of Aspergillus niger; surface fermentation, where the
fungus mycelium (*Aspergillus niger*) grows on the surface of the static culture, where the fermentation product is collected; and fermentation by submerged culture, where the fungus develops entirely submerged in the liquid culture under agitation (FIB, 2014).

Citric acid can be separated by liquid-liquid extraction from its fermentation broth (Wennersten, 1983). Liquid-liquid extraction involves the mass transfer of components between two immiscible or partially immiscible liquid phases, the simplest form involving the transfer of a component (solute) between the liquid phases. The transfer of a dissolved component (solute) between the phases can be favored by the addition of agents that favor the separation of phases and/or also by the use of chemical reactions between solute and solvent (Perry et al., 1984).

Liquid-liquid equilibrium data founded in the literature show that simple solvents do not provide high partition coefficients (Mitchell et al., 1987). Only the work presented by Grinberg et al. (1991) reported the use of a simple solvent, 2-butanol, as effective for separating citric acid. The authors reported that, for 2-butanol as a solvent, the partition coefficient of citric acid is approximately 1. The main disadvantage of the system formed by water + citric acid + 2-butanol is that 2-butanol is partially soluble in water in presence of citric acid and, therefore, the region between the two phases is extremely narrow. Lintomen (1999) studied the ternary system water + 1-butanol + citric acid. It was found that this system has a two-phase region and greater selectivity when compared to the ternary system composed of 2-butanol.

Therefore, the aim of this work is to make an evaluation of the liquid-liquid extraction process for the recovery of citric acid, by collecting experimental equilibrium data from the water + 1-butanol + citric acid system, thermodynamic modeling and process simulation.

2 METHODOLOGY

2.1 EXPERIMENTAL DATA

The experimental data of liquid-liquid extraction with mass fractions in the aqueous and organic phases for the water + 1-butanol + citric acid system at temperatures of 5.5°C, 15°C were taken from Pinto's work (2003), and are presented in Tables 1 and 2, respectively.
Table 1. Mass fraction for the water (1) + 1-butanol (2) + citric acid (3) system at 5.5°C.

| Aqueous Phase | Mixing Point | Organic Phase |
|--------------|--------------|---------------|
| w1           | w2           | w3            | w1 | w2 | w3 | w1 | w2 | w3 |
| 0.9181       | 0.0819       | 0             | 0.5002 | 0.4998 | 0 | 0.1823 | 0.8177 | 0 |
| 0.838        | 0.0843       | 0.0777        | 0.4766 | 0.4694 | 0.054 | 0.2005 | 0.7643 | 0.0353 |
| 0.8142       | 0.0843       | 0.1015        | 0.473 | 0.4554 | 0.0716 | 0.2095 | 0.7417 | 0.0489 |
| 0.7747       | 0.0821       | 0.1431        | 0.4418 | 0.4635 | 0.0947 | 0.2191 | 0.7224 | 0.0584 |
| 0.7216       | 0.0859       | 0.1925        | 0.4358 | 0.4251 | 0.1391 | 0.2628 | 0.9339 | 0.1033 |
| 0.6393       | 0.1126       | 0.2481        | 0.4128 | 0.3979 | 0.1892 | 0.3292 | 0.5061 | 0.1647 |

Table 2. Mass fraction for the water (1) + 1-butanol (2) + citric acid (3) system at 15°C.

| Aqueous Phase | Mixing Point | Organic Phase |
|--------------|--------------|---------------|
| w1           | w2           | w3            | w1 | w2 | w3 | w1 | w2 | w3 |
| 0.922        | 0.078        | 0             | 0.495 | 0.506 | 0 | 0.191 | 0.809 | 0 |
| 0.848        | 0.083        | 0.069         | 0.478 | 0.476 | 0.046 | 0.208 | 0.762 | 0.03 |
| 0.787        | 0.076        | 0.137         | 0.459 | 0.446 | 0.095 | 0.235 | 0.7 | 0.066 |
| 0.72         | 0.087        | 0.194         | 0.439 | 0.423 | 0.139 | 0.266 | 0.631 | 0.103 |
| 0.645        | 0.107        | 0.249         | 0.419 | 0.395 | 0.186 | 0.323 | 0.525 | 0.152 |

The data at 25°C, on the other hand, were taken from the work of Lintomen et al. (2001) and are presented in Table 3.

Table 3. Mass fraction for the water (1) + 1-butanol (2) + citric acid (3) system at 25°C.

| Aqueous Phase | Mixing Point | Organic Phase |
|--------------|--------------|---------------|
| w1           | w2           | w3            | w1 | w2 | w3 | w1 | w2 | w3 |
| 0.5354       | 0.4646       | 0             | 0.9334 | 0.0666 | 0 | 0.2019 | 0.7981 | 0 |
| 0.5281       | 0.4464       | 0.0255        | 0.8967 | 0.0663 | 0.037 | 0.2143 | 0.7719 | 0.0138 |
| 0.5308       | 0.4259       | 0.0433        | 0.8722 | 0.0661 | 0.0617 | 0.2186 | 0.7588 | 0.0226 |
| 0.5227       | 0.4256       | 0.0517        | 0.8609 | 0.0653 | 0.0738 | 0.2163 | 0.7585 | 0.0252 |
| 0.5867       | 0.339        | 0.0743        | 0.8297 | 0.0651 | 0.1052 | 0.2161 | 0.7421 | 0.0418 |
| 0.4323       | 0.4122       | 0.1555        | 0.7124 | 0.0699 | 0.2177 | 0.2263 | 0.6812 | 0.0925 |

2.2 NRTL THERMODYNAMIC MODEL

The Non-Random Two-Liquid (NRTL) thermodynamic model correlates the activity coefficients ($\gamma$) of a compound with its molar fractions in the liquid phase ($x_i$) and is also based on Gibbs free energy, as shown in Equation (1) (Smith & Van Ness, 1959).

$$ \frac{gE}{RT} = x_1 x_2 \left( \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) $$  (1)
Where \( G_{ji} \) and \( \tau_{ji} \) are given by Equations (2) and (3), respectively.

\[
G_{ji} = e^{-\alpha_{ji}\tau_{ji}} \tag{2}
\]

\[
\tau_{ji} = \frac{A_{ji}}{RT} \tag{3}
\]

For a multicomponent system, with several components, the activity coefficient \((\gamma)\) is given by Equation (4).

\[
\ln \gamma_i = \frac{\sum_{j=1}^{n} t_{ji} G_{ji} x_j}{\sum_{l=1}^{n} G_{li} x_l} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{l=1}^{n} G_{lj} x_l} \left( t_{ij} - \sum_{r=1}^{n} t_{ri} G_{ri} x_r \right) \tag{4}
\]

Where \( \alpha_{ji} = \alpha_{ij} \), where:

\( \alpha_{ji}, \tau_{ji} \) and \( \tau_{ij} \) - model parameters;

\( x_j \) - composition of a component \( j \).

\( \gamma_i \) - the activity coefficient.

In this model, the parameters that were adjusted to the experimental data in Tables 1, 2 and 3, were the binary parameters \( A_{ij}, A_{ji} \) and \( \alpha_{ji} \), and the results are shown in Table 4.

| Component i | Component j | \( A_{ij} \) | \( A_{ji} \) | \( \alpha_{ij} \) |
|-------------|-------------|--------------|--------------|--------------|
| Water       | 1-butanol   | 702.62       | 264.73       | 0.38649      |
| Water       | Citric acid | 1840.8       | 2577.6       | 0.20000      |
| 1-butanol   | Citric acid | 1350.5       | -949.67      | 0.23701      |

2.3 THERMODYNAMIC CONSISTENCY OF EXPERIMENTAL DATA

The thermodynamic consistency of the data on the mooring lines was verified through the Othmer-Tobias (Equation (5)) and Hand (Equation (6)) correlations.

\[
\ln \left( \frac{1-w_{33}}{w_{33}} \right) = a + b \ln \left( \frac{1-w_{11}}{w_{11}} \right) \tag{5}
\]

\[
\ln \left( \frac{w_{23}}{w_{33}} \right) = a + b \ln \left( \frac{w_{21}}{w_{11}} \right) \tag{6}
\]
Where $w_{33}$, $w_{23}$, $w_{11}$ and $w_{21}$ correspond to:

- $w_{33}$: mass fraction of 1-butanol in the organic phase;
- $w_{23}$: mass fraction of citric acid in the organic phase;
- $w_{11}$: mass fraction of water in the aqueous phase;
- $w_{21}$: mass fraction of citric acid in the aqueous phase.

With Equations (5) and (6), the graphs of $\ln\left(\frac{1-w_{33}}{w_{33}}\right)$ versus $\ln\left(\frac{1-w_{11}}{w_{11}}\right)$ (Othmer-Tobias) and $\ln\left(\frac{w_{23}}{w_{33}}\right)$ versus $\ln\left(\frac{w_{21}}{w_{11}}\right)$ (Hand) were plotted on the Origin v.8 software. A linear trend line was inserted and evaluated how close to 1 was the value of the correlation coefficient ($R^2$). For the thermodynamic data to be considered consistent, the adjustment of these graphs must be as close as possible to a line.

2.4 TERNARY GRAPHICS

The ternary graphs were plotted in ORIGIN v.8 and the results obtained from mass fraction calculated using the NRTL thermodynamic model, using the TML program, were compared to the experimental data.

The deviations for each tie line were calculated according to Equation (10):

$$\text{Deviation}\% = \frac{\text{Experimental} - \text{Calculated}}{\text{Experimental}} \times 100 \quad (10)$$

Relative and average deviations were also calculated, Equations (11) and (12), respectively.

$$\text{Relative deviation}\% = \left(\frac{\sigma_m}{\bar{X}}\right) \times 100 \quad (11)$$

$$\text{Average deviation} \% = \frac{\sum_{i=1}^{n} |d_i|}{n} \quad (12)$$

Where:

- $\sigma_m$ = Standard deviation;
- $\bar{X}$ = Average of the individual deviations;
- $d_i$ = Individual deviation;
n = Number of data.

2.5 PROCESS SIMULATION

The simulation of liquid-liquid extraction was carried out in the Aspen Plus V8.8 simulator. Figure 1 corresponds to the simulated flowchart.

Figure 1. Flowchart simulated in Aspen Plus.

Where:

FEED: diluted stream of citric acid;
SOLVENT: stream with pure solvent;
EXTRACT: extract stream, concentrated citric acid, mixed with the solvent;
RAFFINAT: stream of raffinate, containing the water that was separated.

The EXTRACT block was used to simulate a liquid-liquid extraction column.

The NRTL thermodynamic model was used, and the parameters $A_{ij}$ and $A_{ji}$ calculated from the mathematical code program contained in the TML were inserted.

The operating specifications of the EXTRACT block were taken from Pinto (2003) according to Table 6.

Table 6. Operational data for the simulation of the liquid-liquid extraction column.

| Feed (12% water + 88% citric acid, mass fractions) | 100 kg/h |
| Solvent (1-butanol) | 100 kg/h |
| Stages | 5 |
| Temperature | 25°C |
| Pressure | 1 atm |
Sensitivity analysis was performed by varying the amount of solvent in the feed from 100 kg/h to 1800 kg/h, with a response to the flow of citric acid in the extract stream for each of these variations, in order to find the amount of 1-butanol that extracts the highest percentage of citric acid from the feed stream.

Two analyzes were performed, one for a 12% water + 88% citric acid feed and the other for a 50% water + 50% citric acid feed.

The economic analysis was performed to verify the maximum profit of the process, according to Equations (7) - (9).

\[
\text{Profit (}/\$/\text{year}) = (\text{Receipt - Costs}) \times 8760 \quad (7)
\]

\[
\text{Receipt} = \dot{V}_{\text{extract}}^{\text{Citric acid}} (kg/hr) \times P_{\text{Citric acid}} (\$/kg) \quad (8)
\]

\[
\text{Costs} = \dot{V}_{\text{fed}}^{1-\text{butanol}} (kg/hr) \times P_{1-\text{butanol}} (\$/kg) \quad (9)
\]

The multiplication factor in Equation (7) corresponds to the number of hours that a year contains.

The prices of the components used are shown in Table 7:

| Component   | Price ($/kg) |
|-------------|--------------|
| 1-Butanol   | 0.02751      |
| Citric acid | 4.492        |

Source: Chemical book¹; Fisher Scientific².

A graph of the amount of solvent in kg/h versus the annual value of the receipt, costs and profit was plotted and it was evaluated for which solvent flow the profit was maximum.

3 RESULTS AND DISCUSSION

3.1 EXPERIMENTAL DATA CONSISTENCY TEST

The consistency test was performed with both models, Othmer-Tobias and Hand, the graphs were plotted for the experimental data for three temperature ranges. Linearized the
experimental data according to Equations (5) and (6) and the graphs were plotted to evaluate the experimental consistency.

The Othmer-Tobias and Hand graphs for temperatures of 5.5°C, 15°C and 25°C are shown in Figures 2 to 4.

Figure 2. Graphs of linearization of experimental data using the (A) Othmer-Tobias and (B) Hand model at 5.5°C.

Figure 3. Graphs of linearization of experimental data using the (A) Othmer-Tobias and (B) Hand model at 15°C.
Figure 3. Graphs of linearization of experimental data using the (A) Othmer-Tobias and (B) Hand model at 25ºC.

Table 8 has the angular (a) and linear (b) coefficients and the value of $R^2$ generated by the linearization calculated by the ORIGIN v.8 for each of the lines in Figures 2 to 4.

| Correlation       | Othmer-Tobias | Hand     |
|-------------------|---------------|----------|
| Temperature (ºC)  | a  | B       | $R^2$    | a  | b       | $R^2$    |
| 5,5               | 0.77811       | 0.20049  | 0.84741  | 1.29164 | -0.17239 | 0.95304  |
| 15                | 0.70513       | 0.17377  | 0.92396  | 1.29967 | -0.03293 | 0.996262 |
| 25                | 0.57372       | -1.01875 | 0.34229  | 1.36807 | -0.05044 | 0.99097  |

According to the results presented in Table 8, we observed that the Hand model was the best fitted the three temperatures, with an $R^2$ close to 1, indicating a good thermodynamic consistency of the experimental data.

The fact that one model performed better than the other is due to the limitations of each correlation, having an influence on factors such as system miscibility, the number of components, operating temperature, among others.
3.2 TERNARY GRAPHICS AND TIE LINES

The results obtained by TML using the NRTL thermodynamic model for the water (1) + 1-butanol (2) + citric acid (3) system, in the three temperatures, are shown in Tables I, II and III in Appendix, together with their individual deviation from experimental and calculated data on molar fractions.

The symbols $X_i^{\text{Exp}}$ and $X_i^{\text{Calc}}$ correspond to the experimental and calculated molar fraction of the component, respectively.

Results related to the calculations of the relative deviations and the average absolute are presented in Tables 9, 10 and 11.

Table 9. Relative and average absolute deviation for the water (1) + 1-butanol (2) + citric acid (3) system data at 5.5° C.

| Component  | Relative Deviation (%) | Average Deviation (%) |
|------------|------------------------|-----------------------|
| 1-Butanol  | 1,1476                 | 15,3207               |
| Citric acid| 0,2651                 | 16,0987               |
| Water      | 0,7410                 | 2,8657                |

Table 10. Relative and average absolute deviation for the water (1) + 1-butanol (2) + citric acid (3) system data at 15° C.

| Component  | Relative Deviation (%) | Average Deviation (%) |
|------------|------------------------|-----------------------|
| 1-Butanol  | 1,2322                 | 13,6760               |
| Citric acid| 0,2949                 | 19,0169               |
| Water      | 0,8231                 | 2,4000                |

Table 11. Relative and average absolute deviation for the water (1) + 1-butanol (2) + citric acid (3) system data at 25° C.

| Component  | Relative Deviation (%) | Average Deviation (%) |
|------------|------------------------|-----------------------|
| 1-Butanol  | 0,9065                 | 14,9617               |
| Citric acid| 0,1389                 | 7,2247                |
| Water      | 0,6023                 | 2,3601                |

Evaluating the relative deviations and the average absolute deviations, was noted that the data set at 25° C present the smallest deviations and thus, a greater precision.

The average absolute deviations of the data at 5.5° C and 15° C were higher than expected, which is justified by the fact that this type of deviation corresponds to the average of the
distances between each data, which gives us a notion of the variability in a data set. Therefore, the farther one data is from the other, the greater its deviation.

With the results of the experimental and calculated mass fractions, ternary graphs were plotted for the system studied at temperatures of 5.5°C, 15°C and 25°C, as shown in Figure 5.

Figure 5. Ternary graph for the water system (1) + 1-butanol (2) + citric acid (3) at (A) 5.5 °C, (B) 15 °C and (C) 25 °C

Evaluating the ternary graphs and Tables 9, 10 and 11, it was concluded that the system at 25°C, presented the least difference between the experimental and the calculated data, therefore, this temperature was established for operating the simulation of the liquid-liquid extraction process in Aspen Plus.

In all graphs of the Figure 5 and in Tables 8, 10 and 12, it was noted that the smallest errors are in the organic phase, because it is the region that has the largest mass fractions, decreasing the experimental error and, consequently, the variability of the data sets, approaching them.

3.3 PROCESS SIMULATION

The results obtained for a preliminary simulation with an input stream containing 12% Citric Acid and 100 kg/h solvent are shown in Table 12.
Table 12. Results of the simulation for 100 kg/h of 1-butanol and 12% citric acid in feed stream.

| Mass flow of the component (kg/h) | FEED | SOLVENT | EXTRACT | RAFFINAT |
|----------------------------------|------|---------|---------|----------|
| 1-Butanol                        | 0,0000 | 100,0000 | 100,0000 | 0,0000 |
| Citric acid                      | 12,0000 | 0,0000 | 3,3104 | 8,6896 |
| Water                            | 88,0000 | 0,0000 | 0,0000 | 88,0000 |

| Mass fraction of component       | FEED | SOLVENT | EXTRACT | RAFFINAT |
|----------------------------------|------|---------|---------|----------|
| 1-Butanol                        | 0,0000 | 1,0000 | 0,9680 | 0,0000 |
| Citric acid                      | 0,1200 | 0,0000 | 0,0320 | 0,0899 |
| Water                            | 0,8800 | 0,0000 | 0,0000 | 0,9101 |

Table 12 shows that practically all citric acid is found in the raffinate stream, that is, the extraction was not carried out efficiently, can be explained by the small flow of solvent feed into the process.

Figure 6 corresponds to the sensitivity analysis of the variation in the flow rate of 1-butanol in the process feed as a function of the amount of citric acid extracted.

In Figure 6, there is a tendency for the greater the amount of solvent, the greater the amount of citric acid extracted. It is noticed that with 900 kg/h of 1-butanol it is possible to extract all the citric acid that was feed, in other words, above this solvent flow we would only be increasing the costs of the process, without having any increase in receipt. This fact shows...
the importance of the simulation process, with a simple sensitivity analysis it is possible to see which operational point is more suitable for the extraction.

Even though these results are interesting about the process, we cannot fail to notice that a very large variation in solvent flow, such as from 450 to 900 kg/h, shows a small variation in the amount of citric acid extracted. Which leads us to question whether it is really feasible to spend 900 kg/h of 1-butanol to obtain such a small increase in the amount of acid extracted when compared to 450 kg/h of 1-butanol.

The answer for this question can only be obtained from the economic analysis of the process, presented in Figure 7, where there is a variation of 1-butanol according to the profit, receipt, and annual costs of the process.

Figure 7. Variation of 1-butanol (kg/h) in the SOLVENT stream as a function of profit, receipt, and process costs ($/year), for a feed stream with 12% acid.

In Figure 7, it can be seen that at 500 kg/h of 1-butanol, the profit is maximum, 321000 $/year, that is, it is economically more viable to use this amount of solvent to extract 11.23 kg/h of acid, than using 900 kg/h and extracting 12 kg/h.

Thus, the amount of solvent used to simulate the process was 500 kg/h, and the results of the simulation for this solvent flow are shown in Table 13.
Table 13. Simulation results for 500 kg/h of 1-butanol and 12% citric acid in feed stream.

| Mass flow of the component (kg/h) | FEED | SOLVENT | EXTRACT | RAFFINAT |
|----------------------------------|------|---------|---------|----------|
| 1-Butanol                        | 0,0000 | 500,0000 | 500,0000 | 0,0000 |
| Citric acid                      | 12,0000 | 0,0000 | 11,2298 | 0,7702 |
| Water                            | 88,0000 | 0,0000 | 0,0000 | 88,0000 |

| Mass fraction of component       |       |         |         |          |
| 1-Butanol                        | 0,0000 | 1,0000 | 0,9780 | 0,0000 |
| Citric acid                      | 0,1200 | 0,0000 | 0,0220 | 0,0087 |
| Water                            | 0,8800 | 0,0000 | 0,0000 | 0,9913 |

The same simulated procedures for feeding with 12% acid were performed for the case in which this current corresponded to 50% acid. Therefore, Figure 8 corresponds to the sensitivity analysis of the variation in the flow rate of 1-butanol in the process feed as a function of the amount of citric acid extracted.

Figure 8. Variation of 1-butanol (kg/h) in the SOLVENT stream as a function of the amount of citric acid (kg/h) in the EXTRACT stream, 50% acid in feed stream.

The same behavior of Figure 6 was observed in Figure 8, the increase in the amount of solvent increases the amount of acid extracted, reaching the maximum extraction in 600 kg/h of 1-butanol.

To evaluate the amount of optimum solvent from an economic point of view, in Figure 9, there is the variation of 1-butanol according to the profit, receipt and annual costs of the process.
In Figure 9 can be seen that at 400 kg/h of 1-butanol, the profit is maximum, 1,835,241.25 $/year, that is, it is economically more viable to use this amount of solvent to extract 49.11 kg/h of acid, than using 600 kg/h and extracting 50 kg/h.

Therefore, the amount of solvent used to simulate the process was 400 kg/h, and the results of the simulation for this solvent flow are shown in Table 14.

| Mass flow of the component (kg/h) | FEED | SOLVENT | EXTRACT | RAFFINAT |
|----------------------------------|------|---------|---------|----------|
| 1-Butanol                        | 0.0000 | 400.0000 | 400.0000 | 0.0000 |
| Citric acid                      | 50.0000 | 0.0000 | 49.1097 | 0.8903 |
| Water                            | 50.0000 | 0.0000 | 0.0000 | 50.0000 |

Comparing the amounts of solvent needed for the two simulated cases, it was already expected that the feed stream containing 50% acid would require less solvent to have an economically viable extraction. This is because a greater amount of citric acid is being fed, making the wort more concentrated and less difficult to extract.
Comparing the profits for both cases, 321000 $/year for 12% acid in the feed stream and 1,835,241,25 $/year for 50% of acid, it is visible that the profit for the second case is much higher, since uses less solvent to carry out the process.

However, it is worth noting that the evaluation of the costs of this process is a prior estimate, since the simulated extraction is part of a larger process, which did not encompass the route behind obtaining the citric acid supply stream, that is, we do not know whether the costs involved in obtaining a 50% acid stream are worth it compared to the 12% stream.

This shows that the work to obtain the operating points of a process, where not only one variable is taken into account, but a set of many others, which sometimes constitute a tradeoff, that is, an economic action that aims to solve one problem but entails another, forcing a choice on the part of the engineer.

4 CONCLUSIONS

The parameters of the NRTL thermodynamic model were adjusted to the experimental liquid-liquid data, representing the studied system well. The interpretation of the ternary graphs referring to the three temperatures for the studied system, showed the existence of a small heterogeneous region with low mass fractions, which resulted in some high percentages of average deviations, since a small difference in decimal places, already considerably increases the experimental error. The Aspen Plus simulation allowed an overview of the extraction column, making it possible to evaluate some operating variables and their importance in the process. Even with this simulation an economically viable process has been obtained, it is still necessary to evaluate other parameters, to reach more accurate conclusions regarding the process.

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### APPENDIX

Table I. Experimental and calculated data of the mass fractions and individual deviations for the water (1) + 1-butanol (2) + citric acid (3) system at 5.5 °C.

| X1 Exp | X1 Calc | D (%) | X2 Exp | X2 Calc | D (%) | X3 Exp | X3 Calc | D (%) |
|--------|---------|-------|--------|---------|-------|--------|---------|-------|
| 0.9798 | 0.8879  | 0.0212| 0.1221 | 475.58907 | 0.0000 | 0.0000 | 0.0000 |
| 0.9679 | 0.8955  | 0.0237| 0.1029 | 334.64301 | 0.0084 | 0.0016 | 80.6183 |
| 0.9645 | 0.9000  | 0.0243| 0.0975 | 301.81294 | 0.0113 | 0.0025 | 78.1721 |
| 0.9587 | 0.9041  | 0.0247| 0.0922 | 273.59255 | 0.0166 | 0.0036 | 78.1457 |
| 0.9488 | 0.9072  | 0.0275| 0.0875 | 218.72495 | 0.0237 | 0.0053 | 77.6748 |
| 0.9266 | 0.8954  | 0.0397| 0.0854 | 115.37686 | 0.0337 | 0.0192 | 43.0902 |
| 0.4784 | 0.4806  | 0.5216| 0.5194 | 0.4179608 | 0.0000 | 0.0000 | 0.0000 |
| 0.5147 | 0.5238  | 0.4768| 0.4581 | 3.9300394 | 0.0085 | 0.0181 | 112.4706 |
| 0.5312 | 0.5391  | 0.4571| 0.4372 | 4.3707479 | 0.0116 | 0.0238 | 104.4712 |
| 0.5475 | 0.5574  | 0.4388| 0.4125 | 5.9824969 | 0.0137 | 0.0301 | 119.7955 |
| 0.5262 | 0.5793  | 0.4545| 0.3840 | 15.502255 | 0.0194 | 0.0367 | 89.3299 |
| 0.7039 | 0.6910  | 0.2630| 0.2536 | 3.5889442 | 0.0330 | 0.0554 | 67.6658 |

Table II. Experimental and calculated data of the mass fractions and individual deviations for the water (1) + 1-butanol (2) + citric acid (3) system at 15° C.

| X1 Exp | X1 Calc | D (%) | X2 Exp | X2 Calc | D (%) | X3 Exp | X3 Calc | D (%) |
|--------|---------|-------|--------|---------|-------|--------|---------|-------|
| 0.9798 | 0.8877  | 0.0202| 0.1213 | 499.65398 | 0.0000 | 0.0000 | 0.0000 |
| 0.9696 | 0.8954  | 0.0231| 0.1033 | 347.2932  | 0.0073 | 0.0013 | 81.6327 |
| 0.9616 | 0.9070  | 0.0227| 0.0891 | 293.20688 | 0.0157 | 0.0039 | 75.4297 |
| 0.9484 | 0.9106  | 0.0277| 0.0816 | 194.51065 | 0.0239 | 0.0079 | 67.0293 |
| 0.9291 | 0.9012  | 0.0373| 0.0820 | 119.55532 | 0.0336 | 0.0169 | 49.7170 |
| 0.4926 | 0.4848  | 0.5074| 0.5152 | 1.5253636 | 0.0000 | 0.0000 | 0.0000 |
| 0.5248 | 0.5206  | 0.4681| 0.4632 | 1.0446932 | 0.0071 | 0.0163 | 128.0505 |
| 0.5716 | 0.5635  | 0.4135| 0.4046 | 2.1571947 | 0.0149 | 0.0319 | 113.5877 |
| 0.6205 | 0.6100  | 0.3570| 0.3456 | 3.2041228 | 0.0225 | 0.0444 | 97.3310 |
| 0.6944 | 0.6803  | 0.2749| 0.2651 | 3.5473895 | 0.0307 | 0.0546 | 77.6260 |
Table III. Experimental and calculated data of the mass fractions and individual deviations for the water (1) + 1-butanol (2) + citric acid (3) system at 25°C.

| X₁ Exp | X₁ Calc | D (%) | X₂ Exp | X₂ Calc | D (%) | X₃ Exp | X₃ Calc | D (%) |
|-------|---------|-------|-------|---------|-------|-------|---------|-------|
| 0.8258 | 0.8795 | 6.4978 | 0.1742 | 0.1205 | 30.8072 | 0.0000 | 0.0000 | 0.0000 |
| 0.8265 | 0.8863 | 7.2454 | 0.1698 | 0.1133 | 33.2921 | 0.0037 | 0.0004 | 89.5722 |
| 0.8315 | 0.8907 | 7.1210 | 0.1622 | 0.1086 | 33.0229 | 0.0064 | 0.0007 | 88.9937 |
| 0.8284 | 0.8922 | 7.6994 | 0.1639 | 0.1070 | 34.7261 | 0.0077 | 0.0008 | 89.1927 |
| 0.8678 | 0.8982 | 3.5042 | 0.1219 | 0.1003 | 17.6992 | 0.0103 | 0.0015 | 85.7420 |
| 0.7902 | 0.9096 | 15.1023 | 0.1831 | 0.0864 | 52.8313 | 0.0267 | 0.0041 | 84.7337 |
| 0.5100 | 0.4890 | 4.1176 | 0.4900 | 0.5110 | 4.2857 | 0.0000 | 0.0000 | 0.0000 |
| 0.5315 | 0.5005 | 5.8383 | 0.4653 | 0.4934 | 6.0391 | 0.0032 | 0.0061 | 91.2773 |
| 0.5396 | 0.5088 | 5.6972 | 0.4552 | 0.4810 | 5.6633 | 0.0052 | 0.0102 | 94.8375 |
| 0.5367 | 0.5119 | 4.6190 | 0.4574 | 0.4765 | 4.1623 | 0.0059 | 0.0116 | 98.1229 |
| 0.5397 | 0.5264 | 2.4772 | 0.4505 | 0.4558 | 1.1721 | 0.0098 | 0.0179 | 82.7198 |
| 0.5650 | 0.5700 | 0.8938 | 0.4134 | 0.3965 | 4.0812 | 0.0217 | 0.0335 | 54.5958 |