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Liquid-liquid equilibrium for water furfural extraction using different solvents and temperatures in the software aspen plus

Equilíbrio líquido-líquido para extração de furfural da água usando diferentes solventes e temperaturas no software aspen plus

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Brazilian Journal of Development

ABSTRACT

The thermodynamic study of liquid-liquid equilibrium (LLE) can provide insights for understanding the process of furfural extraction of water by extraction in biorefinery plants, which produces high value-added products. The present work aimed to use the LLE of the water (1) + fufural (2) + solvent (3) system from experimental data and computer modeling for simulation or liquid-liquid extraction behavior using different solvents, verifying its efficiencies. The solvents studied were p-xylene, toluene, benzyl alcohol, acetophenone and methyl isobutyl. The thermodynamic NRTL model was able to monitor well the studied system. With a simulation run on Aspen Plus®, verify that the system adopted is an economically viable process.

Key words: biorefinarias, computacional simulation, liquid-liquid extraction

RESUMO

O estudo termodinâmico do equilíbrio líquido-líquido (ELL) pode fornecer subsídios para compreensão do processo de extração do furfural da água por extração em plantas de biorefinarias, que fornecem produtos de alto valor agregado. O presente trabalho teve como objetivo utilizar estudar o do ELL do sistema água (1) + fufural (2) + solvente (3) a partir de dados experimentais e modelagem computacional para simular o comportamento da extração líquido-líquido com o uso de diferentes solventes, verificando suas eficiências. Os solventes estudados foram o p-xyleno, tolueno, álcool benzílico, acetofenona e metil isobutil. O modelo termodinâmico NRTL conseguiu representar bem o sistema estudado. Com a simulação realizada no Aspen Plus® verificou-se que o sistema proposto é um processo economicamente viável.

Palavras-chave: biorefinarias, simulação computacional, extração líquido-líquido

1 INTRODUCTION

Industrial processes in general must be projects to achieve the best efficiency of the proposed system. As support for the detection of the best scenarios, experimental data and computer simulations can be used by the design engineers. Biorefineries are plants developed for the extraction of biofuels and chemical components of high added value from biomass. Knowing and optimizing your processes are fundamental tasks in the new context of the bioeconomy (MONCADA et al., 2016).

Biomass is composed of fractions of cellulose, lignin and hemicellulose, in addition to ash. In order to improve the obtainment of products derived from it, pre-treatment operations are usually necessary, in order to better the actions of agents on its components. One of the basic chemicals that can be obtained from biorefineries is furfural (ZANG et al., 2020).

It is a highly versatile and key derivative for the manufacture of a range of industrial chemicals of commercial interest, such as: use in the refining of lubricants, such as fungicides,

Brazilian Journal of Development

bactericides, etc. can be produced in the temperature range between 413.15K and 458.15K and pressure between 3.5 and 10 atm. It can be obtained through azeotropic distillation, which is very expensive and has high energy consumption; supercritical CO2 extraction, still in the experimental phase; adsorption and membrane separation, limited according to the concentration of the solution and mass; and through liquid-liquid extraction. This last process is the most suitable for industrial scale, due to the lower cost, lower energy expenditure and level of efficiency. Furfural has limited solubility in water, about 8.3% by weight at a temperature of 293.15K. This aspect favors the choice of the liquid-liquid extraction process since the solute tends to go to the solvent easily (XIN et al., 2016).

The traditional furfural production process involves reaction, distillation unit and extraction. The pre-treated biomass is introduced in the reactor, in which hydrolysis reactions occur, obtaining about 6% of furfural, 90% of water and 4% of other products (acetic acid / methanol) (XING et al., 2011). In a current context, we seek to work with advanced biorefineries that are more efficient and use less energy, thus justifying research on the stages of this production.

The mixture of the solute, the diluent and the solvent should be carefully studied in order to understand how will the extraction process and, therefore, it uses thermodynamic study of the liquid-liquid equilibrium (LLE) of the ternary mixture solute-furfural, diluent-water and solvent. It is possible to determine the fractions present in the extract and raffinate of each component of the mixture (STEPHAN et al., 2018).

The present work aims to study the LLE of the water (1) + fufural (2) + solvent (3) system from experimental data, applying to biorefinery systems. Seven different solvents were studied and simulation of the industrial separation process was carried out on AspenPlus®.

2 METHODOLOGY

The experimental data that based the work developed are shown in Table 1. The experiment was developed at atmospheric pressure and at different temperature levels, as indicated.

Brazilian Journal of Development

Table 1. Solvents and temperatures used

N	Solute	Diluent	Solvent	T (K)
01	Furfural	Water	P-Xylene	298,15
02	Furfural	Water	Toluene	298,15
03	Furfural	Water	P-Xylene	323,15
04	Furfural	Water	Toluene	323,15
05	Furfural	Water	Benzyl Alcohol	323,15
06	Furfural	Water	Acetophenone	323,15
07	Furfural	Water	Methyl isobutyl carbinol	298,15

The first part of the work was the elaboration of the ternary diagrams of the studied systems. Next, LLE data prediction was checked using NTRL modeling, using the ChemCad 7.0® software. Both results were compared from the perspective of process efficiency in relation to parameters D and S, calculated by Equations 1 and 2.

$$D = \frac{x_{2b}}{x_{2a}} \tag{1}$$

$$S = \frac{x_{2b}/x_{1b}}{x_{2a}/x_{1a}} \tag{2}$$

Where:

D → Efficiency

S → Separation Factor

X_{2a} → Fraction of the solute in the aqueous phase

X_{1a} → Diluent fraction in the aqueous phase

X_{2b} → Fraction of the solute in the organic phase

X_{1b} → Diluent fraction in the organic phase

The operating conditions for the extractor were removed from the work of Pokki et al. (2018) and simulated in the ASPEN Plus software. Temperature data and extraction solvents were taken from the work of Xin et al. (2016).

Brazilian Journal of Development

2.1 MODEL UNIQUAC

The UNIQUAC model (Universial Quasi-Chemical) is a method of determining the activity coefficient used to describe the phase equilibrium. It is based on the theory of statistical mechanics used by Gunggenheim in his quasi-chemical theory for non-random molecules of mixtures containing components of different sizes.

2.2 PROCESS SIMULATION

The simulation of liquid-liquid extraction was carried out in the Aspen Plus V10 simulator. Figure 1 corresponds to the simulated flowchart.

Figure 1. Simulated flowchart in Aspen Plus
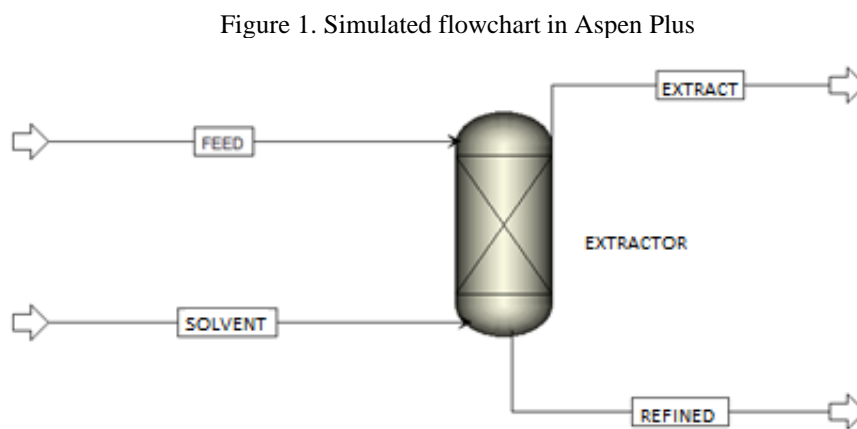
Where each chain in Figure 1 corresponds to:

FEED: diluted furfural current;

SOLVENT: current with pure solvent;

EXTRACT: extract stream, concentrated furfural, mixed with solvent;

REFINED: stream of raffinate, containing the water that was separated.

The *EXTRACT* block was used to simulate a liquid-liquid extraction column. The UNIQUAC thermodynamic model was used.

Table 2. Operational conditions for simulating the liquid-liquid extraction column in ASPEN Plus

Feed (28,57% water + 71,43 % furfural)	1000 kmol/h
Solvent	1000 kmol/h
Stages	7
Temperature	298,15 K and 323,15 K
Pressure	1 atm

Brazilian Journal of Development

3 RESULTS AND DISCUSSIONS

The ternary diagrams of the experimental data were elaborated and can be seen in Figure 2. It is noticed that the region of interest is different for each solvent. When the same solvents were tested under different temperature conditions, there was no significant variation in the extraction capacity, which will be expressed by the efficiency factors.

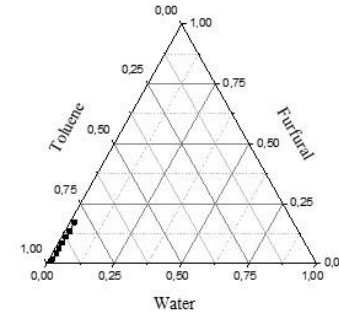Figura 2. Ternary diagrams obtained from LLE experimental data

(a) water (1) + furfural (2) + p-xylene (3) at 298,15 K

(b) water (1) + furfural (2) + p-xylene (3) a 323,15 K
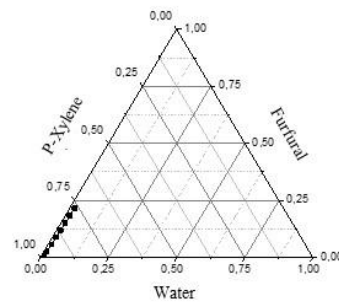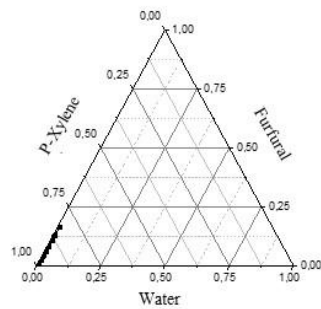
(c) water (1) + furfural (2) + toluene (3) at 298,15 K
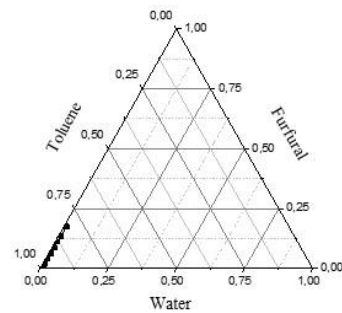
(d) water (1) + furfural (2) + toluene (3) at 323,15 K

(e) water (1) + furfural (2) + benzyl alcohol (3) at 323,15 K

(f) water (1) + furfural (2) + acetophenone (3) at 323,15K
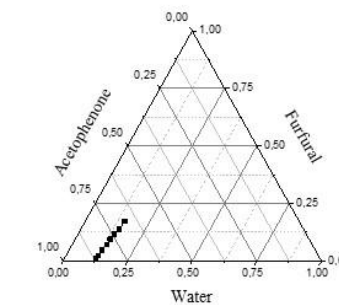
The diagrams obtained from the data prediction using the NTRL model are shown in Figure 3. The predictive capacity of the model was verified, including the fact of predicting

Brazilian Journal of Development

the complete LLE curve of the process, expanding the range of information beyond experimental data. Again, in solvents with tests at different temperatures, similarity in the extraction capacity was verified.

Figure 3. Ternary diagrams obtained from NTRL modeling data

(a) water (1) + furfural (2) + p-xylene (3) at 298,15 K

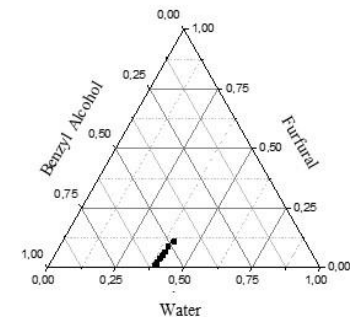(b) water (1) + furfural (2) + p-xylene (3) at 323,15 K

(c) water (1) + furfural (2) + toluene (3) at 298,15 K

(d) water (1) + furfural (2) + toluene (3) at 323,15 K

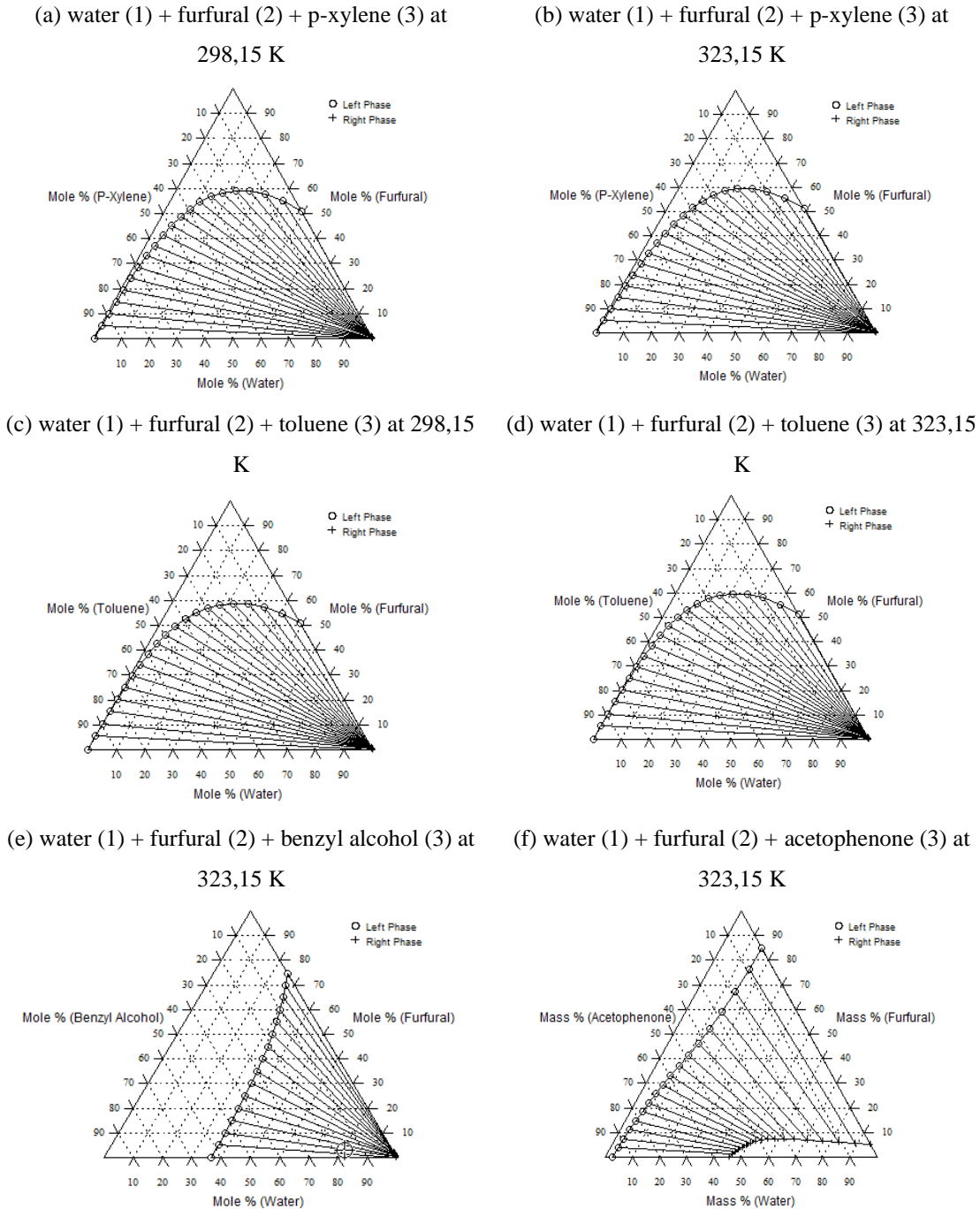(e) water (1) + furfural (2) + benzyl alcohol (3) at 323,15 K

(f) water (1) + furfural (2) + acetophenone (3) at 323,15 K

Brazilian Journal of Development

The extraction efficiency was compared and the data shown in Table 2. It appears that it is not prudent to compare the values of D and S obtained from the molar fractions obtained experimentally and in modeling, since among solvents there is a significant discrepancy. However, an observation can be made from the perspective of the best removal process. Thus, the scale of better solvent extraction capacity can be obtained. The highest levels of efficiency and extraction factor obtained were p-Xylene and Toluene in both situations.

Table 3. LLE efficiency parameters

Solvent	X_{2b}	D_{exp}	D_{cal}	S_{exp}	S_{cal}
P-Xylene – 298,15 k	0.1641	30.96	136.9363	3666	16128.58
Toluene – 298,15 k	0.1744	37.91	136.9436	3810	15067.84
P-Xylene – 323,15 k	0.2157	32.68	40.30	1854	14347.08
Toluene – 323,15 k	0.1718	35.79	40.34795	2094	26382.62
Benzyl Alcohol – 323,15 k	0.1103	16.97	66.28746	40.48	137.4138
Acetophenone – 323,15 k	0.1717	49.06	3.73701	319.4	42.48094

NOTE: Exp: Calculated from experimental data. Cal: Calculated from data obtained through NTRL modeling

The following solvents were simulated: p-xylene (298.15 and 323.15 K), toluene (298.15 and 323.15 K) and methyl isobutyl carbinol (298.15 K). Table 4 and 5 shows the results for p-xylene at 298.15 K and 323.15 K, respectively.

Table 4. Results of simulation of furfural-water + p-xylene at 298.15 K

Mass flow of the component in kg/hr	FEED	SOLVENT	EXTRACT	REFINED
Furfural	285.7	0	160.3108	316.9647
Water	714.3	0	5.956674	680.5478
P-xylene	0	1000	783.9098	168.2179
Mass fraction of component	**FEED**	**SOLVENT**	**EXTRACT**	**REFINED**
Furfural	0.2857	0	0.168717	0.271902
Water	0.7143	0	0.006269	0.583795
P-xylene	0	1	0.825014	0.144303

Brazilian Journal of Development

Table 5. Results of simulation of furfural-water + p-xylene at 323.15 K

Mass flow of the component in kg/hr	FEED	SOLVENT	EXTRACT	REFINED
Furfural	285.7	0	277.1042	8.595755
Water	714.3	0	2.56404	711.736
P-xylene	0	1000	999.8149	0.185122
Mass fraction of component	FEED	SOLVENT	EXTRACT	REFINED
Furfural	0.2857	0	0.216575	0.01193
Water	0.7143	0	0.002004	0.987813
P-xylene	0	1	0.781421	0.000257

From the results presented it can be seen that for the temperature of 323.15 K there was a better separation obtaining 98% water in the raffinate stream.

Table 6 and 7 show the results for toluene at 298.15 K and 323.15 K, respectively.

Table 6. Results of simulation of furfural-water + toluene at 298.15 K

Mass flow of the component in kg/hr	FEED	SOLVENT	EXTRACT	REFINED
Furfural	285.7	0	207.1295	78.57048
Water	714.3	0	1.393987	712.906
Toluene	0	1000	999.3841	0.615871
Mass fraction of component	FEED	SOLVENT	EXTRACT	REFINED
Furfural	0.2857	0	0.171478	0.099194
Water	0.7143	0	0.001154	0.900029
Toluene	0	1	0.827368	0.000778

Table 7. Results of simulation of furfural-water + toluene at 323.15 K

Mass flow of the component in kg/hr	FEED	SOLVENT	EXTRACT	REFINED
Furfural	285.7	0	284.7993	0.900715
Water	714.3	0	2.279682	712.0203
Toluene	0	1000	999.5393	0.460717
Mass fraction of component	FEED	SOLVENT	EXTRACT	REFINED
Furfural	0.2857	0	0.221355	0.001263
Water	0.7143	0	0.001772	0.998092
Toluene	0	1	0.776873	0.000646

Brazilian Journal of Development

As in the result for p-xylene using the solvent toluene, the temperature of 323.15 K obtained better values of composition improving the extraction of Furfural obtaining 99.8% of water from the raffinate stream.

Table 8 shows the results for the methyl isobutyl carbinol solvent.

Table 8. Results of simulation of furfural-water + methyl isobutyl carbinol 298.15 K

Mass flow of the component in kg/hr	FEED	SOLVENT	EXTRACT	REFINED
Furfural	285.7	0	285.3272	0.372757
Water	714.3	0	82.23813	632.0619
MIC	0	1000	990.9129	9.087141
Mass fraction of component	FEED	SOLVENT	EXTRACT	REFINED
Furfural	0.2857	0	0.210034	0.000581
Water	0.7143	0	0.060537	0.985254
MIC	0	1	0.729429	0.014165

As with other solvents, methyl isobutyl carbinol has been shown to be effective in extracting Furfural by obtaining high separation values.

Comparing the values of furfural composition in the feed stream with that obtained in the extract stream we have the percentage of furfural extracted from the water shown in Table 9.

Table 9. Percentage of furfural removed in the solvent

Solvent	Percentage of Furfural extracted from water
P-xylene (298,15 K)	56,11%
P-xylene (323,15 K)	96,99%
Toluene (298,15 K)	72,49%
Toluene (323,15 K)	99,68%
Methyl isobutyl carbinol (298,15 K)	99,86%

Comparing the values in Table 9, we see that the methyl it-butyl carbinol obtained a higher percentage of extraction, but its value was very similar to that of toluene at 323.15 K and, therefore, a previous economic analysis of the process must be carried out to know which will be the most suitable solvent.

Brazilian Journal of Development

4 CONCLUSIONS

This work provided an evaluation of the liquid-liquid extraction process in the recovery of furfural, through the collection of experimental equilibrium data, thermodynamic modeling and process simulation.

The parameters of the NRTL thermodynamic model were adjusted to the experimental liquid-liquid balance data, managing to represent the studied system well.

The Aspen Plus simulation provided 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, in order to reach more accurate conclusions regarding the process.

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