

## Simulation of the Tetrahydrofuran Dehydration Process by Extractive Distillation in Aspen Plus

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### Abstract

The aim of this work is to simulate and analyze an extractive distillation process (extractive distillation and recovery columns) for the separation of Tetrahydrofuran (THF)-Water azeotropic mixture using Aspen Plus® and Aspen Split simulators. Calculation of vapor liquid equilibrium of Tetrahydrofuran–Water–Entrainer system was done using the NRTL model, which binary interaction parameters were regressed using experimental data. A methodology for the study and selection of different candidate entrainers was followed, determining that the most suitable is glycerol. A sensitivity analysis was performed to estimate the variables to be used in the simulation, establishing that the entrainer to feed ratio and the entrainer feed stage are determinant to obtain high purity THF. The entrainer feed temperature does not assure a high concentrated distillate, but is a significant parameter on the extractive column energy consumption. Certain values for the reflux ratio produce maximum THF composition in the product, as high reflux ratios would decrease the efficiency of the entrainer. The results obtained with the simulation demonstrate that glycerol decreases heat duty and entrainer consumption, compared to 1,4-butanediol and 1,2-propanediol.

Keywords: Extractive Distillation, Entrainer, Tetrahydrofuran, Azeotrope

### 1. Introduction

Tetrahydrofuran dehydration is a process of special economical concern, as anhydrous THF demand is increasing. THF is a cyclic ether used as a solvent in the manufacture of paint, adhesives, impression ink, pharmaceutical products, etc. It is also an intermediate product and a monomer. THF most important industrial application is the production of Polytetramethylene-glycol (PTMEG), necessary in the elaboration of Spandex Fibres, polyurethane and polyester ether. In the last years the THF market has grown in approximately 5.6% annually (Nexant, 2003).

Most of THF production processes are related to the 1,4-Butanediol (BDO), being the Reppe Synthesis the first to be industrially applied (Murib et al, 1981). Alternative processes have been developed, in which butadiene, alcohols, n-butane, maleic anhydride and maleic acid are used as reagents. From these processes an aqueous THF solution is produced, which have to be dehydrated to 99.9%mol THF (BASF, 2001), for the product to be commercially attractive. Though, THF-Water mixture has an azeotrope in 82.9%mol THF and cannot be separated by conventional distillation. For azeotropic mixtures, several industrially important processes exist, such as: azeotropic distillation, adsorption, pervaporation, pressure swing distillation, extractive distillation using organic entrainers and saline extractive distillation. Extractive distillation using BDO is the most commonly used method for THF dehydration (Xu et al, 2006a).

Simulation is a useful tool to evaluate the process, as some of its characteristics may be predicted avoiding high expenses. The simulation of the extractive distillation process for the THF dehydration is performed with a suitable entrainer, previously selected using an appropriate methodology. To determine the operating variables and their effect on the product purity and energy consumption, a sensitivity analysis was done. Extractive distillation process is described in the next section.

## 2. Extractive Distillation

Extractive distillation includes an entrainer (solvent) to increase the relative volatility of the key components of the feed. This process is used to separate low relative volatility systems, or those that have an azeotrope. The entrainer must have certain characteristics in order for the process to succeed (Van Dyk, 2000).

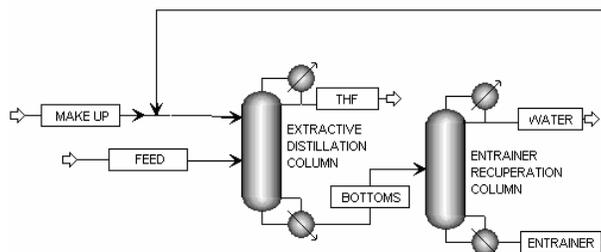


Fig. 1. Extractive Distillation Process

On Fig. 1 the extractive distillation process for THF-Water separation is shown. The azeotropic mixture and the entrainer streams are fed to the extractive distillation column, where the dehydration of the desired compound (THF) takes place. The bottom product of the extractive distillation column feeds the entrainer recovery column, where the entrainer (leaving from the reboiler) is separated from water and is recycled to the extractive distillation column. As part of the entrainer is lost in the process, the recycled stream is mixed with a make up entrainer stream (Seider et al., 2004).

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An extractive distillation entrainer does not form additional azeotropes, which is an advantage. Also, as the recovery column is a totally independent operation, it can serve different columns simultaneously. As the entrainer must accomplish several characteristics, it is usually not environmentally harmful. This technology is well developed, and modelling and simulation of this process is possible.

The recovery column represents high energy consumption. The selection of the solvent is an important limiting variable for some mixtures, as commercial solvents cannot be used in all cases. Reflux ratio for extractive distillation column can show a maximum or a minimum, which limits the process to operate in a very specific range of conditions (Tojo et al, 1993).

### **3. Entrainer Selection**

In this analysis, an entrainer selection methodology is proposed. Literature review was done to make up a procedure to classify and choose suitable entrainers for extractive distillation. In the following sections this methodology is explained on detail.

#### *3.1. Entrainer Selection Criteria*

An entrainer for extractive distillation must have some or all the characteristics listed below (Van Winkle, 1967; Seader, 2006; Pham et al, 1990; Bieker et al., 1993):

1. It must change the relative volatility between the key components of the mixture
2. It must have very low volatility, so that it exits the column as a bottom product.
3. The entrainer must be thermally stable
4. Must not be reactive with none of the components of the mixture.
5. Has to be economically available.
6. For safety and maintenance reasons, it must not be corrosive.
7. Cannot be toxic
8. The entrainer must be easily separated with the other bottom product.
9. Has to be completely miscible with the components of the azeotropic mixture.

The entrainer selection can be based on its ability of modifying the relative volatility of the system. However, the final decision must be taken with an economical evaluation of all the involved variables and criteria, considered along with the selectivity of the entrainer, in order to determine the conditions that minimize the capital investment and operating costs.

The evaluation of the criteria, used to choose the most suitable entrainer, must be done with an appropriate methodology, so it can be made in the most efficient way.

#### *3.2. Entrainer Selection Methodology for Extractive Distillation*

In order to select an entrainer, it is necessary to connect different elements, such as databases, heuristics and numeric routines. The following steps are recommended to be followed:

*Class Selection:* The components of the feed must be classified by their polarity and hydrogen bonding formation.

*Similar Chemical Group Selection:* the entrainer must create differences of polarity between the components of the feed. In this case solubility parameters may be used. In extractive distillation the entrainer should maximize one component solubility and minimize the solubility of the other components of the mixture. Methods to determine selectivity parameters may be used as well (Rodríguez-Donis et al, 2001).

*Useful Entrainers Proposal:* A first selection of the possible entrainers is controlled by different factors: upper and lower limits of boiling point, entrainer miscibility with the other components, azeotropy between the entrainer and the other substances, reactions, etc. In this step the most important tools can be heuristics, empirical approximations, numeric methods, group contribution methods and databases.

*Suitable Entrainer Ranking:* The benefits of the entrainers are classified according to the following characteristics (Van Dyk, 2000):

- Entrainer Selectivity
- Relative Volatility Change
- Miscibility
- Distillate and Residue Products
- Azeotrope Formation with the Azeotropic Feed

Binary and ternary phase equilibrium estimation using group contribution methods or activity coefficient models may be used to see differences between the entrainers. Ternary diagrams, residue curve maps, as well as binary and pseudobinary diagrams are useful to decide which entrainer is the best for the process.

*Other Important Aspects:* Within the most suitable entrainers, other factors have to be analyzed (Bieker et al, 1993).

- Toxicity
- Corrosivity
- Thermal Stability
- Availability and price
- Manipulation Facilities
- Environmental Impact
- Cost reduction possibility (Heat Integration)

Many of the criteria stated above need the estimation of the Vapor-Liquid equilibrium (VLE). It has to be chosen properly, for the simulation to be reliable. In the next section the selection procedure to determine the most suitable thermodynamic model is shown.

### 3.3. Thermodynamic Equilibrium

The thermodynamic model selection for simulation purposes is the most important decision to make. In order to identify the model(s) that predicts properly the thermodynamic equilibrium, heuristics must be applied (Carlson, 1996).

Thermodynamic model analysis should take into account different characteristics and conditions: polarity, electrolyte presence, pressure, binary interaction parameter availability and the need of Liquid-Liquid equilibrium information. Model selection procedure was followed from the algorithm proposed in Aspen Plus® (Carlson, 1996).

Taking into account that all the components (THF, water and entrainer) are polar non-electrolytic compounds, the operating pressure is 1 atm, the binary interaction parameters are available and the liquid-liquid equilibrium is not required, the models that predict the system appropriately are UNIQUAC, NRTL and Wilson.

In order to establish which of the models is to be used in the simulation, the calculated data using Aspen Plus binary interaction parameters were regressed with experimental information of the VLE found with literature review<sup>1</sup>. According to this analysis, the model that describes the equilibrium properly is NRTL. On Table 1, the value of RMSE (Root Mean Square Error), that corresponds to the square root of the sum of the errors (squared) is shown for some binary mixtures studied.

Table 1. RMSE values (Aspen Plus).

Model	THF-Water	DMF-THF	Phenol-THF
Wilson	0.77	1.50	1.50
UNIQUAC	0.62	1.18	1.19
NRTL	0.41	0.91	0.91

As the lowest RMSE values for the mixtures tested belong to the analysis made with NRTL binary interaction model, this is the model that best describes the equilibrium data. In the following section, the entrainers are analyzed using NRTL model in Aspen Plus® and Aspen Split®.

### 3.4. Entrainer Analysis in Aspen Split®

Aspen Split is a useful tool for the entrainer selection in azeotropic and extractive distillation. Following the entrainer selection methodology, exposed on section 3.2, 8 substances were chosen as a result of the first steps. The entrainers are studied in Aspen Split, along with some of the restrictions. The criteria that can be studied with Aspen Split are: boiling point, azeotropy and miscibility. Aspen Split made possible the rejection of three of the analyzed entrainers, reducing the selection to 5 entrainers. In order to make a decision between the rest entrainers, residue curve maps and pseudobinary diagrams must be drawn.

<sup>1</sup> THF-Water (Eizo et al, 1975)  
THF-DMF-Water (Shah, 1970)  
THF-Phenol/Phenol-Water (Rehák et al, 1995)

Table 2. Results of the Entrainer Selection in Aspen Split

Entrainer	BP (°C)	Azeotrope	Possible Entrainer
Dimethylformamide	151,77	No	No
Phenol	181,93	Yes (water)	No
Glycerol (GLY)	287,71	No	Yes
1,4-Butanediol (1,4-BDO)	227,83	No	Yes
1,2-Propanediol (1,2-PDO)	187,72	No	Yes
Isobutil Alcohol	107,68	No	No
Ethylene glycol (EG)	197,09	No	Yes
1,6-Hexanediol (1,6-HDO)	253,14	No	Yes

### 3.5. Residue Curve Maps (RCM)

The need of a method to compare different separation agents in azeotropic and extractive distillation is evident. The residue curve maps are a useful tool in the design and analysis of these separation processes (Doherty, 2001). The topology of these maps determine whether an entrainer is suitable or not for extractive distillation (Jiménez et al, 2001).

One residue curve is a line that shows the change of the composition of the liquid phase with time, in a simple distillation. A residue curve map is the collection of these curves for a determined mixture. These maps contain the same information a phase diagram has, but they are more useful for the understanding and design of distillation systems (Pahm et al, 1990)

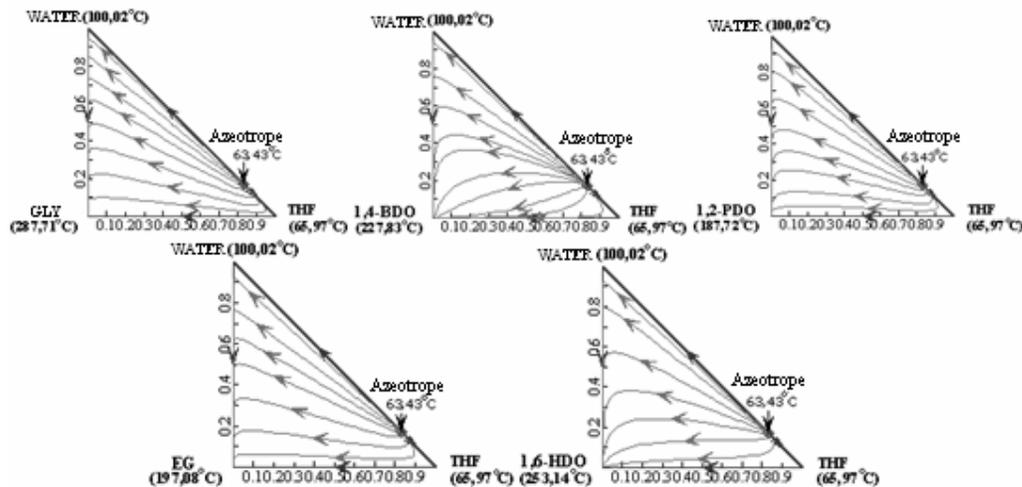


Fig. 2. MCR para la mezcla ternaria THF-Agua-Solvente. P=1 atm (Fuente: Aspen Plus)

Extractive distillation is a separation method that deals with minimum boiling point azeotrope solutions, and a high boiling point entrainer is added. For ternary mixtures, the use of a ternary residue curve map is necessary (triangular shape), where each vertex is labeled with one component. For extractive distillation operations, the stable node (maximum boiling point) must be located in the entrainer vertex, the unstable

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node (minimum boiling point) in the azeotropic point and the two saddle points in the remaining vertexes (Doherty, 2001). Using Aspen Split the residue curve maps are drawn for the entrainers in study. As can be seen in all cases (Fig. 2), the topology of the residue curve maps describes the appropriate configuration for extractive distillation.

### 3.6. Pseudobinary Diagrams in Aspen Split

Pseudobinary diagrams show how relative volatility is affected by the use of an entrainer. On these diagrams, entrainer free mole fractions of the azeotropic mixture are specified in the axes. The relative volatility change is strongly dependent on the Entrainer/Feed ratio (E/F). On Figs. 3 and 4, pseudobinary diagrams are shown, drawn for 30% and 45% entrainer to feed ratio, respectively. The diagrams were sketched using NRTL model to describe the VLE.

From Figs. 3 and 4, the entrainer that would increase the relative volatility of the key components in greater proportion would be glycerol, followed by ethylene glycol and propyleneglycol (1,2-PDO). If 1,4-BDO is used as entrainer, greater entrainer to feed ratio would be needed to break the THF-Water azeotrope. 1,6-hexanediol can be used as entrainer with the entrainer to feed ratios studied, but does not affect the relative volatility as much as glycerol and ethyleneglycol.

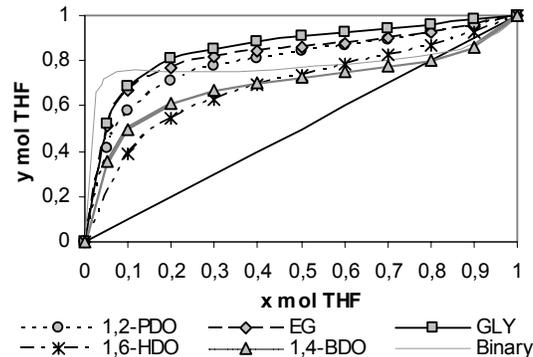


Fig. 3. Pseudobinary Diagram at 30% Entrainer to Feed Ratio (P=1atm)

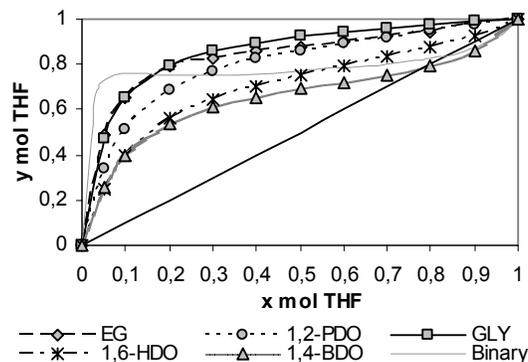


Fig. 4. Pseudobinary Diagram at 45% Entrainer to Feed Ratio (P=1atm)

### 3.7. Other Important Aspects

The cost of the entrainer is an important factor to evaluate, since it is determinant in the economic feasibility of the process. On Table 3, the price of the entrainers is shown.

Table 3. Importing Price of the Entrainers (DIAN, 2006)

Entrainer	Importing Price USD/kg (2006)
Glycerol	0,96
1,4-Butanediol	4,02
Propylene glycol	1,61
Ethylene glycol	0,91
1,6-Hexanediol	1,96

The cheapest entrainer would be ethylene glycol, followed by glycerol and propylene glycol. 1,4-BDO is the most expensive entrainer, and is the one to discard because higher entrainer to feed ratio would be needed to make the separation.

The environmental impact and industrial safety factors of these entrainers are similar, except for the ethylene glycol, which is considerably toxic. As these entrainers all have high boiling point, they have low evaporative emissions to take care about.

The most appropriate entrainer to use in the THF dehydration is glycerol. Even though ethylene glycol is also suitable and has the lowest price, smaller amounts of glycerol would be needed and is less toxic. In the following section the simulation in Aspen Plus is performed, determining the proper operating conditions with a sensitivity analysis. The results obtained in this work will be compared to the results given in other investigations.

## 4. Simulation Results and Analysis

Before the simulation is run in Aspen Plus it is necessary to establish the operating conditions. To do so, a sensitivity analysis should be done, in order to determine which values of some parameters are the ones that give the highest purity in the distillate with moderate energy consumption (condenser and reboiler duty). Aspen Plus has a useful tool to perform this type of analysis. In the next section the sensitivity analysis is explained deeply.

### 4.1. Sensitivity Analysis

The sensitivity analysis is done using Aspen Plus as a tool to evaluate different variables over the THF distillate composition, as well as the condenser and reboiler duty in the extractive column. The variables listed below were tested:

- Number of ideal stages (NS)
- Reflux mole ratio (RR)
- Feed stage (FS)
- Entrainer feed stage (EFS)
- Entrainer feed temperature (EFT)
- Entrainer to feed molar ratio (E/F)

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In Table 4 the azeotropic feed conditions are shown. The feed enters the column with the azeotropic composition at 1 atm, in its bubble point temperature.

Parameter	Value
Feed Mole Flow (kmol/h)	100
Temperature (°C)	63,4
Pressure (atm)	1
Composition (%mol)	
THF	82.9
Water	17.1
Minimum Mole Recovery %	98

To establish the general configuration of the extractive distillation column (number of stages, feed stage, entrainer feed stage and reflux ratio), these variables are studied simultaneously. In Fig. 5, the number of stages and the reflux ratio were analyzed.

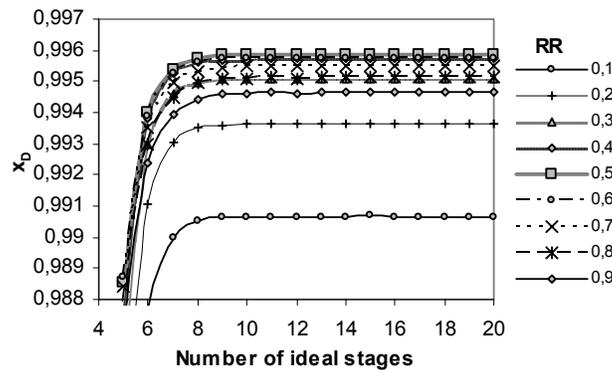


Fig. 5. Influence of the number of stages and reflux ratio in THF mole composition of the distillate (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

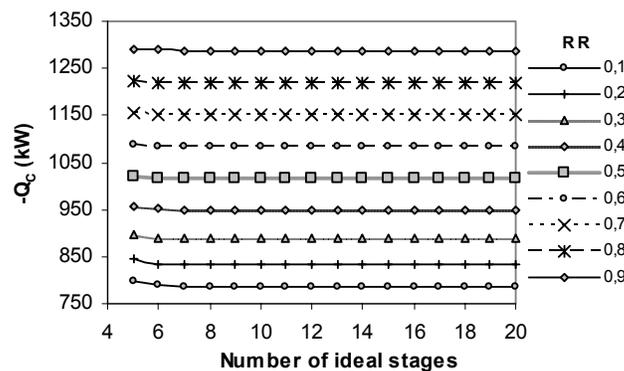


Figure 6. Influence of the number of stages and reflux ratio in the condenser duty (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

As can be seen on Fig. 5 the reflux ratio that gives the highest distillate is 0,5. Moreover, columns with the number of ideal stages greater than 10, give the same

THF mole composition in the distillate, in all the studied cases. That means that a 10 stage column with a reflux ratio of 0,5 would separate the azeotropic mixture satisfactorily. On Figs. 6 and 7 the energy (reboiler and condenser) duty is analyzed using the same variables. As can be seen, for a determined reflux ratio the condenser and reboiler duty do not have changes for different stage number columns. Though, the reflux ratio is important in the column energy consumption: at higher reflux ratio, greater condenser and reboiler duty.

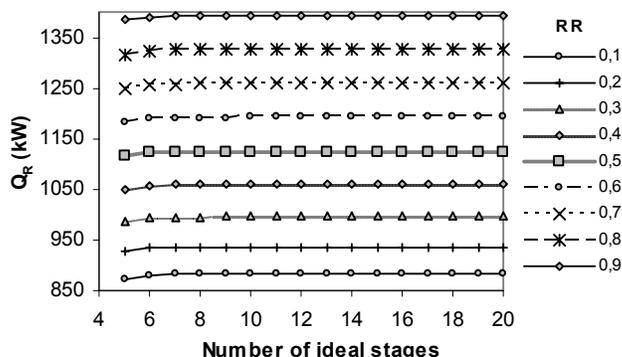


Figure 7. Influence of the number of stages and reflux ratio in the reboiler duty (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

On Figures 8 to 10 THF-Water mixture feed stage and the number of stages influence is studied. A similar behavior with the number of stages is observed: columns with more than 10 stages show similar curves. On Fig. 8 it is shown that for any stage number column, if the feed is below the sixth stage, the THF composition in the distillate is greater than 99.95%. A similar behaviour is exposed on Figs. 9 and 10, where the influence of the feed stage and the number of stages is analyzed over the condenser and reboiler duties. Therefore, in a column with 10 ideal stages, it is adequate to feed the azeotropic mixture on stage 6.

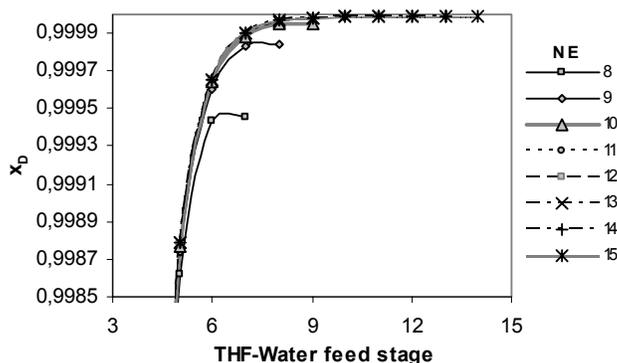


Figure 13. Influence of the number of stages and the feed stage in THF mole composition of the distillate (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

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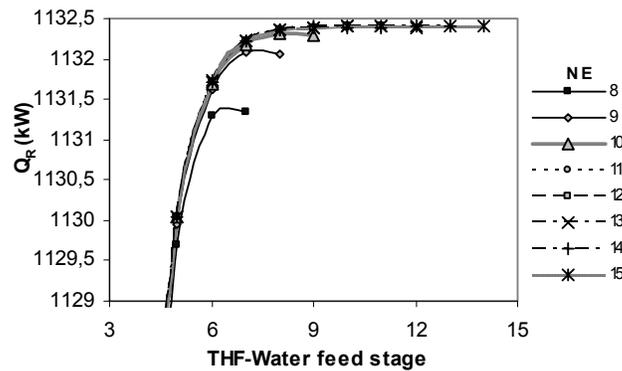


Fig. 9. Influence of the number of stages and the feed stage in the reboiler duty (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

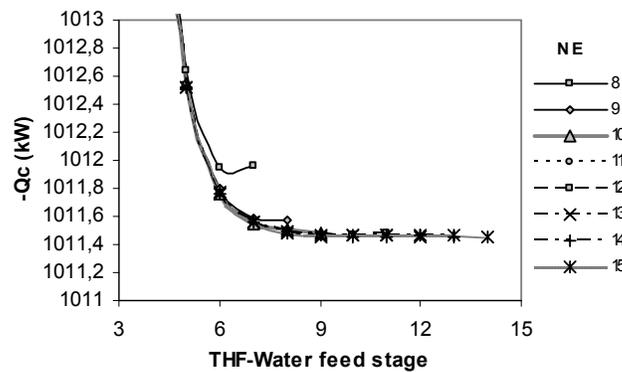


Fig. 10. Influence of the number of stages and the feed stage in the condenser duty (EFS: 2; EFT: 80°C; E/F: 0.3; FS: 4)

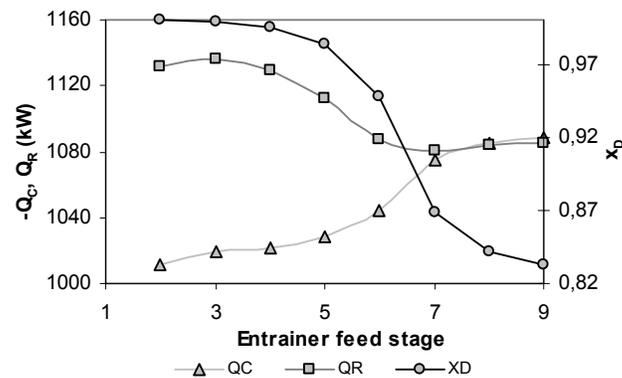


Fig. 11. Influence of the entrainer feed stage on the product purity and energy duty (FS: 6; EFT: 80°C; E/F: 0.3; RR: 0.5; NS: 10)

On Figure 11 the studied variable is the entrainer feed stage. According to the present results this is a determinant variable in the distillate THF composition. If the entrainer is fed in the first stages of the column, the composition of THF in the

distillate is high, because it will be constantly in contact with the vapor. The reboiler and condenser duties are also affected by this variable, having more energy consumption in the condenser when the entrainer is fed in the lower part of the column. The opposite case is seen for the reboiler duty. If the entrainer is fed in the lower zone of the column, higher vapor flow is going to be condensed in the first stage, so the condenser duty increases. If the entrainer is fed in the upper zone of the column, the liquid flow increases as water from the vapor phase is transferred to the liquid phase. Considering this analysis, the entrainer should be fed in the top of the column (stage 2).

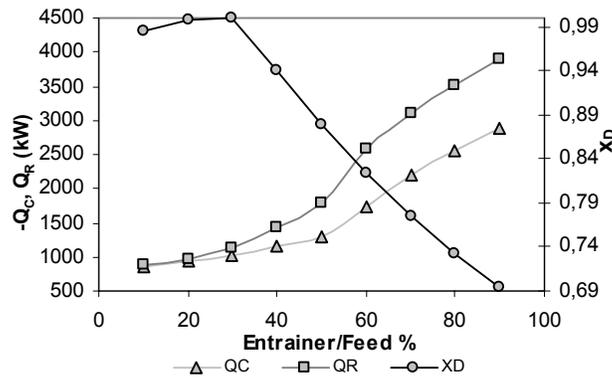


Fig. 12. Influence of the entrainer to feed ratio on the product purity and energy duty (FS: 6; EFS: 2; EFT: 80°C; RR:0.5; NS:10)

On Fig. 12 the entrainer to feed molar ratio is studied. A maximum composition of THF in the distillate is obtained with an entrainer to feed ratio of 30%. The cause of this uncommon behavior is the type of mixture THF-Water-Glycerol is. There are several solutions which relative volatility, in presence of a third component, does not show a linear tendency (Van Winkle, 1967). Condenser and reboiler duties increase when greater entrainer to feed ratio is used. When more entrainer is introduced to the column, liquid flow increases and so the reboiler duty. The most suitable entrainer to feed ratio would be 30%.

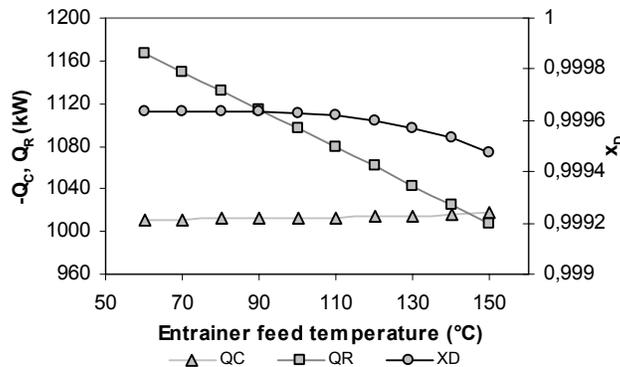


Fig. 13. Influence of the entrainer feed temperature on the product purity and energy duty (FS: 6; EFS: 2; E/F: 0.3; RR: 0.5; NS: 10)

On Fig. 13 the variable under analysis is the entrainer feed temperature. This variable is not dramatically influent in the distillate composition of THF. If the entrainer is fed at a higher temperature, the reboiler duty decreases significantly, while the condenser duty slightly increases. If the entrainer is fed at low temperatures, more energy is needed in the reboiler to evaporate part of the liquid in the column. The condenser duty is higher when the entrainer is introduced to the column at high temperatures, due to an increment on the vapor flow, caused by the evaporation of water from the liquid to the vapor phase. This evaporation is a consequence of introducing the entrainer at very high temperature.

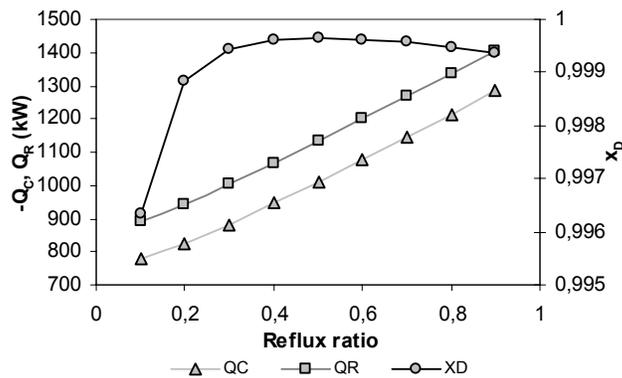


Fig. 14. Influence of the reflux ratio on the product purity and energy duty (FS: 6; EFS: 2; S/A: 0.3; TAS: 80°C; NE: 10)

Finally, on Fig. 14 the reflux ratio is studied, showing the maximum THF composition in the distillate at 0,5. This happens because the vapor phase is THF rich and when it is condensed and refluxed, it dilutes the liquid phase. This dilution makes the entrainer less effective, and the distillate THF composition decreases. The condenser and reboiler duties, both increase with the reflux ratio. As more reflux is used, the liquid phase is higher and the reboiler duty augments. The condenser duty increases because less water is transferred to the liquid phase when more reflux ratio is used.

The sensitivity analysis gives the operating conditions of the extractive distillation column, while the configuration of the entrainer recovery column were determined with a shortcut calculation module in Aspen Plus. These data are shown on Table 5.

#### 4.2. Process Simulation Results

The process to be simulated in Aspen Plus, has two columns: the extractive distillation column (ED) and the entrainer recovery column (ER). The main parameters of the extractive distillation column were determined in the previous section. The main characteristics of the entrainer recovery column were established using Aspen Plus DSTWU (Shortcut Calculation) model to calculate the reflux ratio, the number of stages and the feed stage. The results of this preliminary simulation, as well as other operating variables, are shown on Table 5.

Table 5. Distillation columns configuration

Parameter	ED	ER
Feed stage	6	3
Entrainer feed stage	2	----
Entrainer feed temperature (°C)	80*	----
Entrainer to feed ratio (%)	30%	----
Reflux ratio	0,5	0,1
Number of ideal stages	10	6
Distillate temperature (°C)	----	15
Residue temperature (°C)	----	210
Distillate flor (kmol/h)	81,9	18,28
Condenser type	Total	Total
Pressure (mmHg)	760	60

\*First iteration

From Table 5, it can be seen that the bottoms would leave the recovery distillation column at a very high temperature. In order to recycle the residue stream from the recovery column to the extractive distillation column, it has to be cooled. On the other hand, the azeotropic feed needs to be preheated to its bubble point before it enters the column. However, the whole recycle stream would evaporate part of the feed. Because of this, part (70%) of the flow from the recycled stream is used for this purpose, bypassing the rest of the flow, to have the adequate temperature of both, entrainer and feed temperature streams. On Fig. 15 the process flowsheet used in the simulation of the THF dehydration is shown.

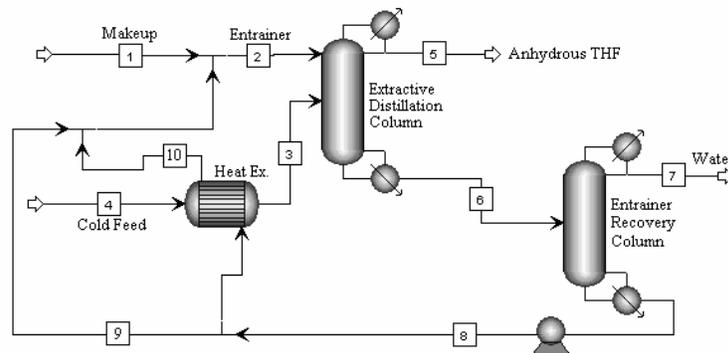


Fig. 15. Process Flowsheet for the extractive distillation system used to dehydrate THF

On Tables 5 and 6 the entering data for the simulation flowsheet shown on Figure 18 is given. The distillation columns are simulated with RADFRAC routine, being the information on Table 5 necessary for the run.

Table 6. Entering Streams Conditions

	1	4
T (°C)	20	20
P (atm)	1	1
Mole Flow (kmol/h)	0,178	100
THF	0	82.9
Water	0	17.1
Glycerol	0,178	0

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The simulation was run in Aspen Plus satisfactorily. The mass and energy balance results are shown on Table 7.

Table 7. Mass and energy balance results

Variable	1	2	3	4	5	6	7	8	9	10
Temperatura °C	20	120,5	63,4	20	65,9	120,7	11,3	208,0	208,0	80
Presión bar	1,013	1,013	1,013	1,013	1,013	1,013	0,08	0,08	0,08	0,08
Fracción de Vapor	0	0	0	0	0	0	0	0	0	0
Flujo Molar kmol/hr	0,18	30	100	100	81,9	48,1	18,3	29,8	8,9	20,9
Flujo Másico kg/hr	16,4	2762,8	6291,1	6291,1	5903,7	3150,3	403,8	2746,4	823,9	1922,5
Flujo Volum. cum/hr	0,01	2,28	83,15	6,94	7,08	2,67	0,40	2,42	0,73	1,54
Entalpía MMkcal/hr	-0,03	-4,64	-5,31	-5,46	-4,12	-5,81	-1,25	-4,46	-1,34	-3,27
Fracción Molar THF	0	0	0,829	0,829	1	0,02	0,06	0	0	0
Agua	0	0	0,171	0,171	0	0,35	0,93	0	0	0
Glicerol	1	1	0	0	0	0,62	0,01	1	1	1

RADFRAC routine is a method that calculates MESH equations in each stage of the column. For this reason, mole flow, compositions and temperature profiles may be drawn. On Figures 16 to 21 show these profiles.

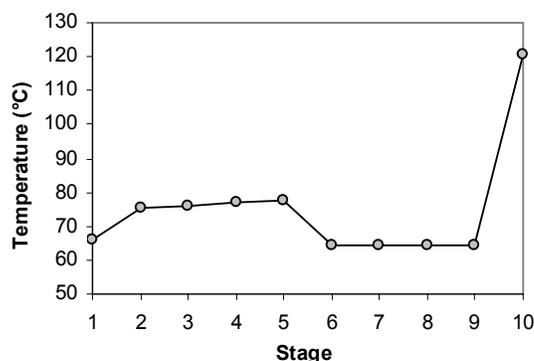


Fig. 16. Extractive Column Temperature Profile

On Figure 16 the temperature profile shows how the temperature changes in the column. There is a temperature augmentation on the second stage, because of the entrainer introduction to the column. On stage 6 the temperature decreases as the azeotropic mixture is fed on that stage. Near to the reboiler the temperature increases dramatically because of the reboiler's heat duty.

On Figure 17 the molar liquid and vapor flows are exposed. As both feeds (entrainer and azeotropic mixture) are introduced in the liquid phase, there is an increase on the liquid molar flow on stages 2 and 6. The vapor flow tends to be constant in the column, except on stage 2. This may happen because the entrainer feed temperature is high and vaporizes some of the water in the liquid phase.

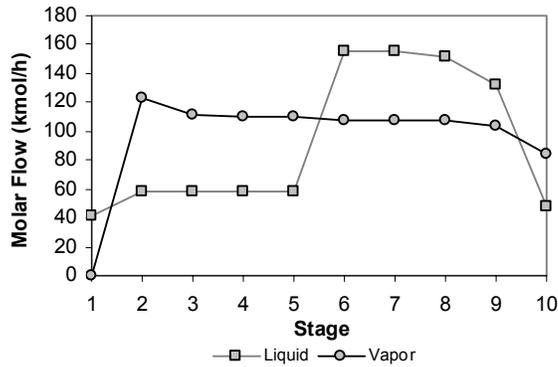


Fig. 17. Column Molar Flow Profile

On Figure 18 the liquid composition profile is shown. The glycerol composition profile has two main changes on stages 2 and 6, where the feeds occur. On the other stages it tends to be constant, while water is being transferred from one phase to the other. The THF composition in the liquid decreases on stage 2 and increases on stage 6. On the first and last stages the composition of the distillate and the residue can be observed, being the former almost THF and the latter a mixture mainly on glycerol and water.

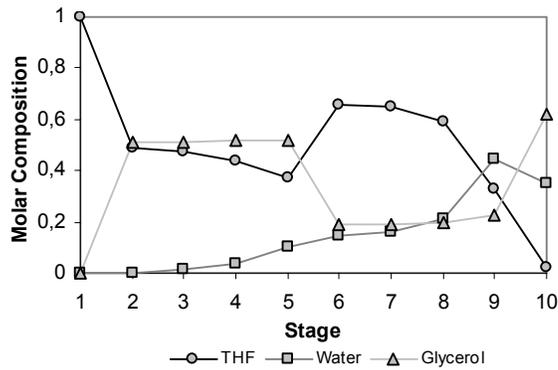


Fig. 18. Column Liquid Composition Profiles

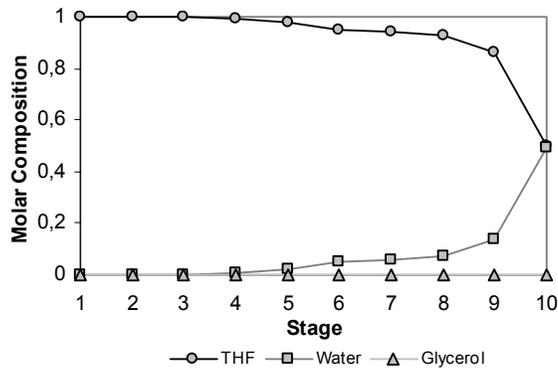


Fig. 19. Column Vapor Composition Profiles

On Figure 19 it is seen that the glycerol is not present in the vapor phase and the main changes occur because of the entrainer's action. In the top stages the vapor phase becomes THF rich, while the water composition decreases. On stage 10, the vapor leaving the reboiler has a composition of approximately 50% THF and 50% water.

On Table 8, the energy consumption of the condenser and the reboiler duties are specified.

Table 8. Condenser and Reboiler Duties on each Column

Heat Duty	ED	ER
Condenser (kW)	-1013,93	-269,98
Reboiler (kW)	1031,17	384,65
Total (kJ/kg of anhydrous THF)	1247,15	399,18

#### 4.3. Comparison to other Studies

Other studies have been done for the THF dehydration process, using other entrainers as separating agents. On Table 9, the obtained results in this study are compared to the ones given in other investigation for 1,2-PDO and 1,4-BDO (Xu et al, 2006b).

Table 9. Results Comparison for the Extractive Column

Parameter	1,2-PDO	1,4-BDO	Glycerol*
THF purity %mol	0,999	0,998	0,9995
ED Reboiler Duty (kJ/kg of anhydrous THF)	1964,22	3649,73	628,79
E/F (mole)	0,6	2	0,3
RR (mole)	0,6	1,2	0,5
ED N.S.	10	10	10
Feed Stage	8	8	6
Entrainer Feed Stage	2	2	2

\*This study

As shown on Table 9 the results obtained in this study demonstrate that the best entrainer to be used in extractive distillation of THF-Water azeotropic mixture is glycerol. The purity of the distillate is comparable between the situations on Table 9, but the other conditions are different. The energy consumption in the reboiler is lower for the extractive distillation with glycerol, while the greatest energy consumption is obtained where 1,4-Butanediol. This is related to the entrainer to feed ratio and the reflux ratio, which are higher for the simulations done with 1,2-propanediol and 1,4-butanediol. These results are comparable as the number of stages and the entrainer feed stage are the same for all the studies.

## 5. Conclusion

A better entrainer for the THF dehydration with extractive distillation was found, developing an appropriate methodology of entrainer selection. Compared to investigations done with 1,4-butanediol and 1,2-propanediol, the use of glycerol as the entrainer assures high THF purity, with less quantity of entrainer and lower heat duty.

The sensitivity analysis gave the most suitable conditions to perform the extractive distillation process with the selected entrainer. The determinant variables in the THF purity are the entrainer to feed ratio and the entrainer feed stage. The entrainer feed temperature does not considerably affect the distillate concentration, but is significant in the energy consumption of the column. The column temperature, molar flow and composition profiles reveal expected behaviours, being closely related to the inlet and outlet mass and energy flows.

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