

SIMULATION OF THE TETRAHYDROFURAN DEHYDRATION PROCESS BY EXTRACTIVE DISTILLATION

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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. The solvent to feed molar ratio, reflux molar ratio, feed stage, feed solvent stage, and feed solvent temperature, were determined and their effects on the separation and the energy consumption in the two columns was studied.

Keywords— Extractive Distillation, Entrainer, Tetrahydrofuran, Azeotrope.

I. INTRODUCTION

Tetrahydrofuran (THF) dehydration is a process of special economical concern, as anhydrous THF demand is increasing. THF is 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, 2004).

Most of THF production processes are related to the 1,4-Butanediol (BDO), being the Reppe Synthesis the first to be industrially applied (Murib and Inskeep, 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, 1999), for the product to be commercially attractive. Though, THF-Water mixture has an azeotrope in 83% mol THF and cannot be separated by conventional distillation.

There is a variety of suitable processes for the separation of azeotropic mixtures, being extractive distillation the most commonly used method for THF dehydration (Xu and Wang, 2006a;b). Extractive distillation uses the addition of a mass separating agent to modify the thermodynamic behaviour of the system. This process

has been studied and applied since the 1950's in laboratories and industries, gaining important attention for its benefits on azeotropic systems separation (Li *et al.*, 2005). For the THF-water mixture, BDO is the most used entrainer for the extractive distillation process (Xu and Wang, 2006a;b).

Simulation is a useful tool to evaluate the process, as some of its characteristics may be predicted without investing too much money. In order to perform a simulation, the type of process and the separating agent must be specified. For an azeotropic mixture, several industrially important processes exist, such as: azeotropic distillation, adsorption, pervaporation (Kozicka *et al.*, 2007), pressure swing distillation, extractive distillation using organic entrainers and saline extractive distillation.

II. EXTRACTIVE DISTILLATION

Extractive distillation includes an entrainer 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 and Niewoudt, 2000).

In 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 recuperation 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 (Perry and Chilton, 2001).

Extractive distillation entrainer does not form additional azeotropes, which is an advantage. Also, as the recuperation column is a totally independent operation, it can serve different columns simultaneously.

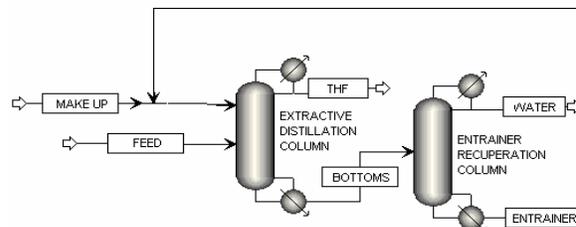


Fig. 1. Extractive Distillation Process.

The entrainer must accomplish several characteristics, so it is usually not environmentally harmful. Like azeotropic distillation, this technology is well developed and hence, modelling and simulation of this process is possible. The recuperation 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).

III. 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 in detail.

A. Entrainer Selection Criteria

An entrainer for extractive distillation must have some or all the characteristics listed below (Van Winkle, 1972):

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 have thermal stability.
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 (Seader, 2006).

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.

B. 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 tool 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 and Niewoudt, 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 can 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 and Simmrock, 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.

C. Thermodynamic Equilibrium

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

Thermodynamic model analysis must 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

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

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	287,71	No	Yes
1,4-Butanediol	227,83	No	Yes
1,2-Propanediol	187,72	No	Yes
Isobutyl Alcohol	107,68	No	No
Ethylene glycol	197,09	No	Yes
1,6-Hexanediol	253,14	No	Yes

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 using experimental information of the VLE found with Literature Review (Sada *et al.*, 1975; Shah and Greene, 1970; Reháč *et al.*, 1995). According to this analysis, the model that describes the equilibrium properly is NRTL. In Table 1, the value of RMSE (Root Mean Square Error), which corresponds to the square root of the sum of the errors (squared) is shown. 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®.

D. Entrainer Analysis in Aspen Split ®

Aspen Split is a useful tool for the entrainer selection for azeotropic and extractive distillation. 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. In Table 2 the results for an analysis made with 8 possible entrainers are shown.

Basically, the boiling point should be 80°C greater than the corresponding to the heavier component (water) and for extractive distillation no formation of additional azeotropes is mandatory. Taking this criterion into account Aspen Split made possible the rejection of three of the analyzed entrainers, reducing the selection to 5 other entrainers. In order to make a decision between the rest entrainers, residue curve maps and pseudobinary diagrams must be drawn.

E. 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 and Malone, 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 composition 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 distillation systems understanding and design (Pahm and Doherty, 1990).

Extractive distillation is a separation method that deals with minimum boiling point azeotrope mixtures, being the entrainer the heaviest component of the mixture. For a ternary mixture, the use of a ternary residue curve map is necessary. In these maps, for extractive distillation operation, the stable node has to be in the entrainer vertex, the unstable node in the azeotropic point and two saddle points corresponding to the azeotropic mixture components vertexes (Doherty and Malone, 2001).

Using Aspen Split the residue curve maps are drawn for the entrainers in study. For all the THF-Water-Entrainer systems under analysis a RCM was drawn, finding the appropriate configuration for extractive distillation in all cases. The RCM for the system THF-Water-Glycerol is shown in Fig. 2.

F. Pseudobinary Diagrams in Aspen Split

Pseudobinary diagrams are obtained by equilibrium calculations taking into account a fixed mole fraction of the entrainer in Aspen Split, which is representative of the internal profile in the extractive distillation column where molar composition is approximately constant in all stages as will be seen in section IV. 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 of the Entrainer/Feed ratio (E/F). An alternative approach to this task, which is based on bifurcation analysis of pinch profiles, is proposed by Brüggemann and Marquardt (2004). In 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 gly-

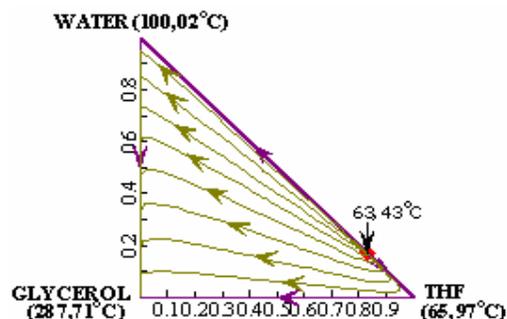


Fig. 2. RCM for THF-Water-Glycerol (P=1atm) Source: Aspen Plus

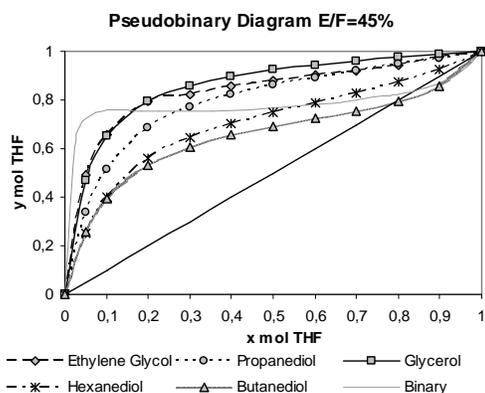


Fig. 3. Pseudobinary Diagram at 30% Entrainer to Feed Ratio (P=1atm) Source: Aspen Plus

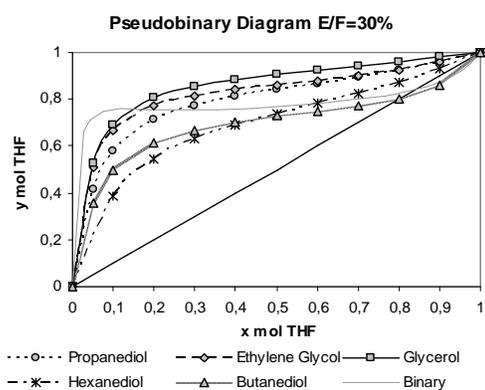


Fig. 4. Pseudobinary Diagram at 45% Entrainer to Feed Ratio (P=1atm) Source: Aspen Plus

Table 3. Importing Price of the Entrainers. Source: 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

col 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 in the entrainer to feed ratios studied, but does not affect the relative volatility as much as glycerol and ethyleneglycol.

G. 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.

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 is the one that would need higher entrainer to feed ratio to make the separation.

The environmental impact and industrial safety factors of these entrainers is 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 done, determining the proper operating conditions to run it with a sensitivity analysis. The results obtained in this work will be compared to the results given in other investigations.

IV. 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 an useful tool to perform these type of analysis (Seider *et al.*, 1999).

In the next section the sensitivity analysis is explained deeply.

A. 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 are the ones tested.

- Number of Stages (NS)
- Reflux Mole Ratio (RR)
- Feed Stage (FS)
- Entrainer Feed Stage (EFS)
- Entrainer Feed Temperature (EFT)
- Entrainer to Feed Molar Ratio (E/F)

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.

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.

As can be seen in Fig. 9 the reflux ratio that gives the highest distillate is 0.5. Moreover, columns with the number of stages greater than 10, give the same THF mole composition in the distillate, for all the cases studied. 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 (condenser and reboiler) duty is analyzed using the same variables. As can be seen, for a determined reflux ratio the condenser

Table 4. Process Design Parameters

Feed Mole Flow (kmol/h)	100
Temperature (°C)	63,4
Pressure (atm)	1
Composition (%mol)	
THF	83
Water	17
Minimum Mole Recovery %	98

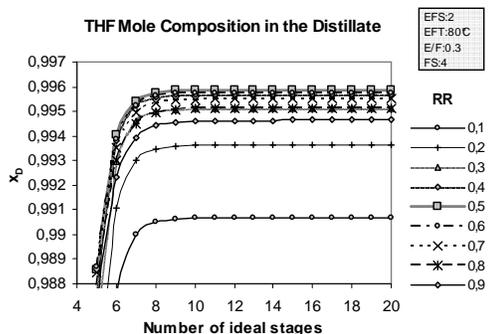


Fig. 5. Influence of the number of stages and reflux ratio in THF mole composition of the distillate. Source: Aspen Plus

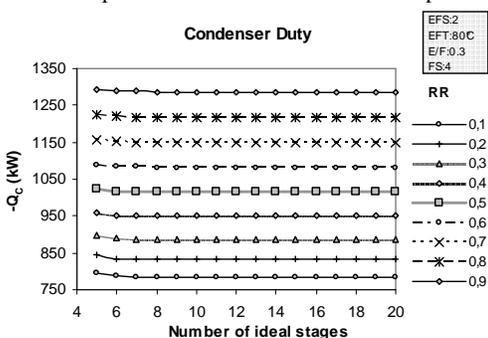


Fig. 6. Influence of the number of stages and reflux ratio on the condenser duty. Source: Aspen Plus

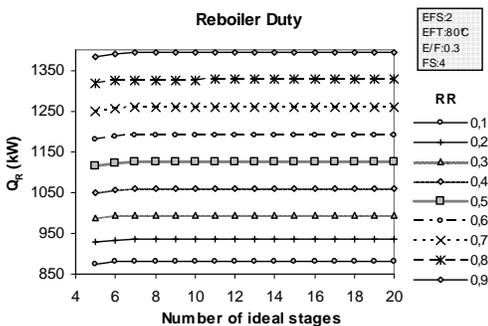


Fig. 7. Influence of the number of stages and reflux ratio on the reboiler duty. Source: Aspen Plus

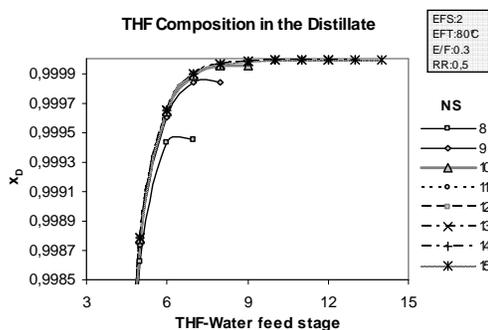


Fig. 8. Influence of the number of stages and the feed stage in THF mole composition of the distillate. Source: Aspen Plus

and reboiler duty do not have changes for different stage number column. Though, the reflux ratio is important

in the column energy consumption: at higher reflux ratio, greater condenser and reboiler duty.

In Figs. 8 to 10 THF-Water mixture feed stage and the number of stages influence is studied. A similar behaviour with the number of stages is observed: columns with more than 10 stages show similar curves.

In 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 Fig. 9 and Fig. 10, where the influence of the feed stage and the number of stages is analyzed over the condenser and reboiler duties.

In Fig 11 the relationship between the reflux ratio and the E/F ratio on the distillate THF composition is exposed. It can be seen that for E/F ratios over 30%, the effect of the reflux ratio is negligible. For E/F ratios lower than 30%, the reflux ratio has greater effect.

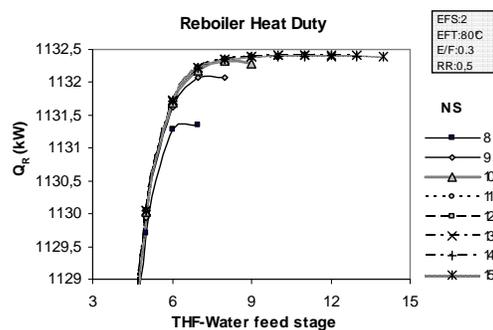


Fig. 9. Influence of the number of stages and the feed stage in the reboiler duty. Source: Aspen Plus

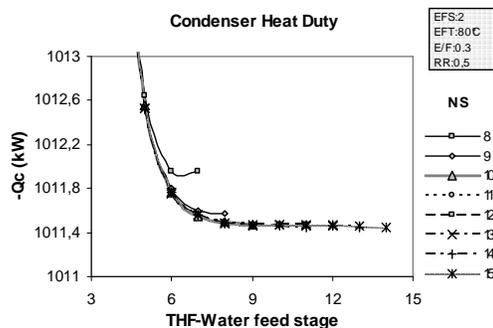


Fig. 10. Influence of the number of stages and the feed stage in the condenser duty. Source: Aspen Plus

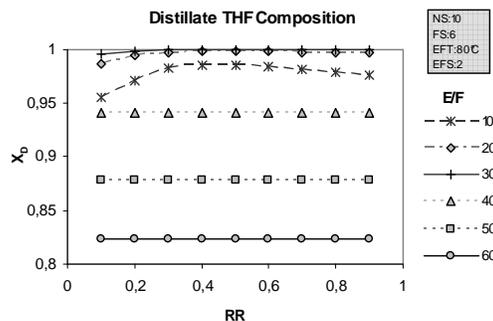


Fig. 11. Influence of the reflux ratio and the E/F (%) ratio on the distillate THF composition. Source: Aspen Plus

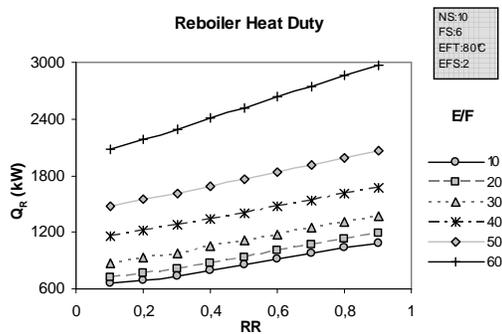


Fig. 12. Effect of the reflux ratio and E/F(%) on the reboiler duty. Source: Aspen Plus.

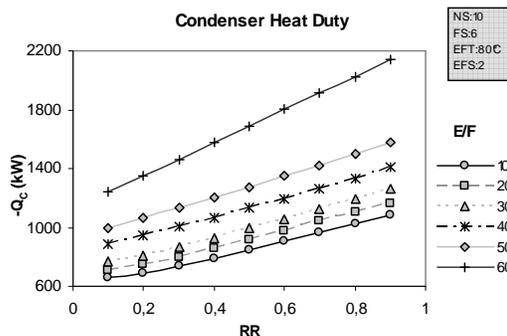


Fig. 13. Effect of the reflux ratio and E/F(%) on the condenser duty. Source: Aspen Plus.

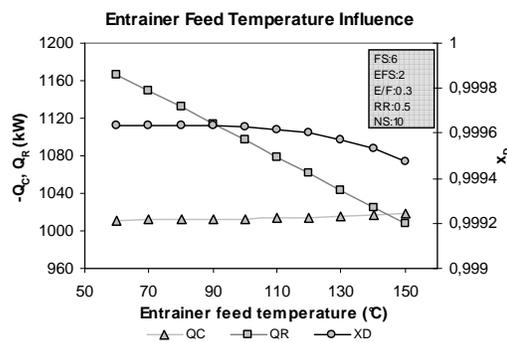


Fig. 14. Influence of the entrainer feed stage on the product purity and energy duty. Source: Aspen Plus

In Figs. 12 and 13, the effect of the reflux ratio and the E/F ratio on the reboiler and condenser duties, respectively, is shown. The heat duty, in both cases, increases when greater reflux ratios and/or E/F ratios are used.

In Fig. 14 the studied variable is the entrainer feed stage. According to the presented 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, as the entrainer flows down the column having contact with the vapour constantly. 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, while the opposite case is seen for the reboiler duty. If the entrainer is fed in the lower zone of the column, higher vapour 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 vapour phase is transferred to the liquid phase.

In Fig. 15 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 behaviour 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, 1972). 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.

In Fig. 16 the variable under analysis is the entrainer feed temperature. This variable is not dramatically influential 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, as the vapour flow may have an increment because one fraction of water is vaporized from the liquid to the vapour phase as a consequence of the high entrainer temperature.

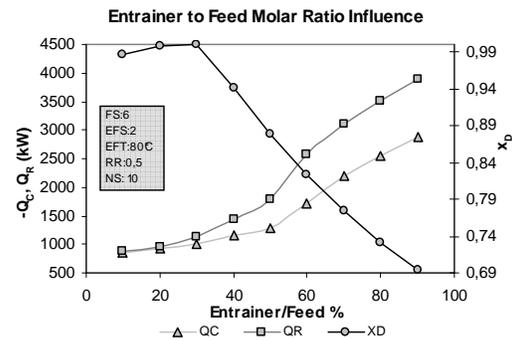


Fig. 15. Influence of the entrainer to feed ratio on the product purity and energy duty. Source: Aspen Plus

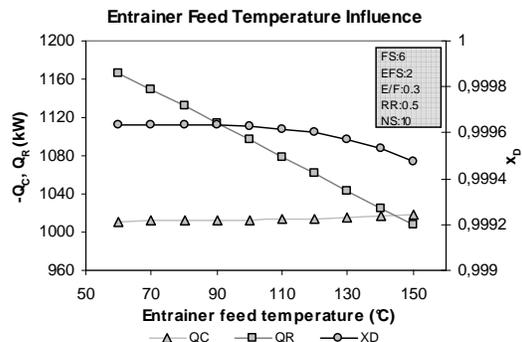


Fig. 16. Influence of the entrainer feed temperature on the product purity and energy duty. Source: Aspen Plus

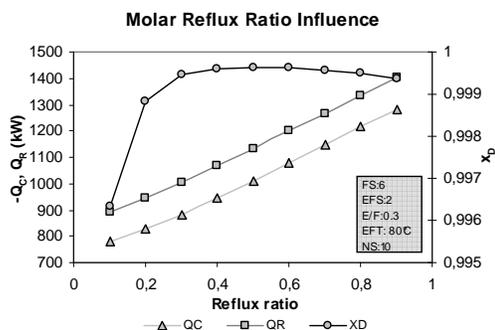


Fig. 17. Influence of the reflux ratio on the product purity and energy duty. Source: Aspen Plus

Table 5. Extractive Distillation Column Configuration

Feed Stage	6
Entrainer Feed Stage	2
Entrainer Feed Temperature (°C)	80*
Entrainer to Feed Ratio (%)	30%
Reflux Ratio	0,5
Number of Stages	10

Table 6. Entrainer Recuperation Column Configuration

Minimum Number of Stages	4
Number of Stages	6
Minimum Reflux Ratio	0,08
Reflux Ratio	0,1
Feed Stage	3
Bottoms Temperature (°C)	210
Distillate Temperature (°C)	15

Finally, in Fig. 17 the reflux ratio is studied, showing the maximum THF composition in the distillate at 0.5. This happens because the vapour 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.

Using the information obtained with the sensitivity analysis, the operating conditions of the process are established (Table 5). These results are used in the simulation explained in the next section.

B. Process Simulation Results

The process to be simulated in Aspen Plus, has two columns: the extractive distillation column (ED) and the entrainer recuperation column (ER). The main parameters of the extractive distillation column were determined in the previous section. The main characteristics of the entrainer recuperation 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 are shown in Table 6.

From Table 6, it can be seen that the bottoms would leave the recuperation distillation column at a very high temperature. In order to use that stream recycled to the extractive distillation column, it has to be cooled. It has

been determined by a previous simulation that the recycle stream is considerably hot and the use of it to pre-heat the feed is inconvenient. However, part (70%) of the flow of the recycled stream can be used for this purpose bypassing the rest of the stream, having the adequate temperature of both, entrainer and feed temperature streams. In Fig. 18 the process flowsheet used in the simulation of the THF dehydration is shown.

In Tables 7 and 8 the entering data for the simulation flowsheet shown in Fig. 18 is given. The distillation columns are simulated with RADFRAC routine, being the information on Table 7 necessary for the run. It is important to observe that in the entrainer recuperation column the bottom temperature should be lower than 220°C in order to avoid thermal degradation of the entrainer, for this reason the column pressure is operated at moderate vacuum. The simulation was run in Aspen Plus satisfactorily. The mass and energy balance results are shown on Table 9.

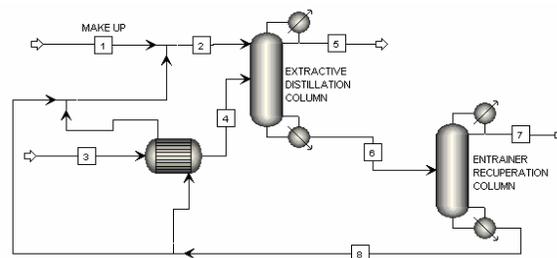


Fig. 18. Process flowsheet for the extractive distillation system used to dehydrate THF. Source: Aspen Plus.

Table 7. Entering Streams Conditions

	1	3
T (°C)	20	20
P (atm)	1	1
Mole Flow (kmol/h)	0,178	100
THF	0	83
Water	0	17
Glycerol	0,178	0

Table 8. Column Configuration

Column Parameters	Column	
	ED	ER
Number of Stages	10	6
Distillate Flow (kmol/h)	81,90	18,28
Molar Reflux Ratio	0,5	0,1
Condenser Type	Total	Total
Feed Stage	6	3
Entrainer Feed Stage	2	----
Pressure (mmHg)	760	60

Table 9. Mass Balance Results

Streams	T	P	Mole Flow	Mole Frac		
				THF	W	Gly
1	20,0	1,01	0,18	0	0	1
2	120,5	1,01	30,0	0	0	1
3	20,0	1,01	100	0,8300	0,1700	0
4	63,4	1,01	100	0,8300	0,1700	0
5	65,9	1,01	81,90	0,9995	0,0004	0
6	120,7	1,01	48,10	0,0240	0,3530	0,624
7	11,3	0,08	18,28	0,0620	0,9280	0,010
8	208,0	0,08	29,82	0	0	1

*T in °C, P in bar, Mole Flow in kmol/h

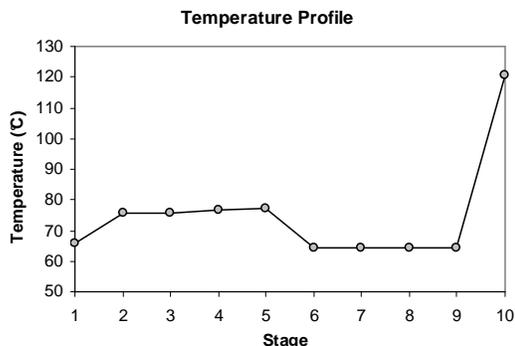


Fig. 19. Extractive Column Temperature Profile Source: Aspen Plus

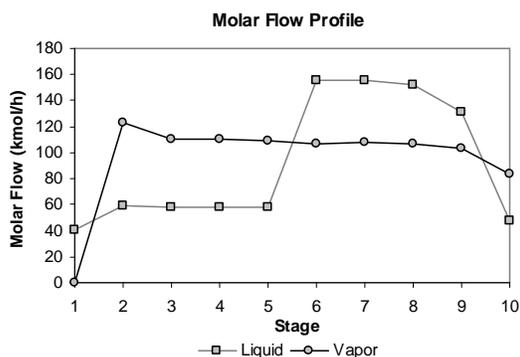


Fig. 20. Column Molar Flow Profile. Source: Aspen Plus

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 Figs. 19 to 22 show these profiles.

In Fig. 19 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. In Fig. 20 the molar liquid and vapour 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 vapour 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.

In Fig. 21 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, as this compound is always present in the liquid phase, 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.

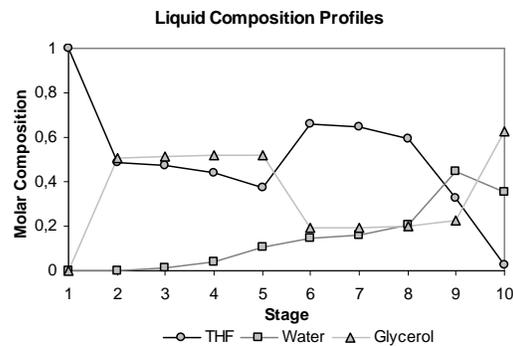


Fig. 21. Column Liquid Composition Profiles. Source: Aspen Plus

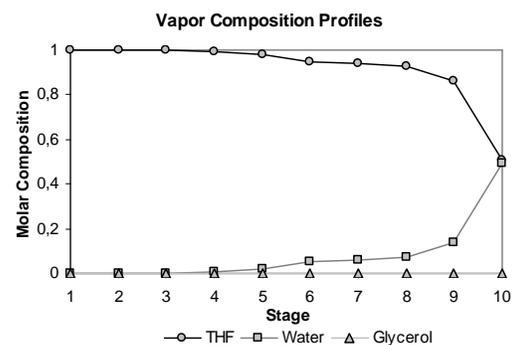


Fig. 22. Column Vapour Composition Profiles. Source: Aspen Plus

In Fig. 22 it is seen that the glycerol is not present in the vapour phase and the main changes occur because of the entrainer's action. In the top stages the vapour phase becomes THF rich, while the water composition decreases. On stage 10, the vapour leaving the reboiler has a composition of approximately 50% THF and 50% water. On Table 10, the energy consumption of the condenser and the reboiler duties are specified.

C. Comparison to other Studies

Other studies have been done for the THF dehydration process, using other entrainers as separating agents. On Table 11, the obtained results in this study are compared to the ones given in other investigation (Xu and Wang, 2006a).

Table 10. Condenser and Reboiler Duties on each Column

Heat Duty	ED	ER
Condenser*	-1013,93	-269,98
Reboiler*	1031,17	384,65
Total**	1247,15	399,18

* Duties in kW; ** Total Duty in kJ/kg of anhydrous THF

Table 11. Results Comparison for the Extractive Column

Parameter	1,2-PDO**	1,4-BDO**	Glycerol
THF purity % mol	0,9990	0,9980	0,9995
ED Reboiler Duty	1964,22	3649,73	628,79
E/F (mole)	0,6	2,0	0,3
RR (mole)	0,6	1,2	0,5
ED N.S.	10	10	10
Feed Stage	8	8	6
E. Feed Stage	2	2	2

*Duty in kJ/kg of anhydrous THF; ** Source: Xu and Wang (2006b)

Table 12. Parameters used in the costing analysis

Efficiency	Assumed 60%
Material	Stainless Steel
No. of connections	6
Type of trays	Bubble Cap
Thickness	5/8 in

Table 13. Results of the costing analysis and comparison.

Equipment	1,2-PDO	1,4-BDO	Glycerol
Shell ID (m)	1,17	1,43	0,95
Reboiler HTA (m ²)	211	240	208
Condenser HTA (m ²)	242	268	234
Column Cost (x10 ³ USD)	374	765	119
Reboiler Cost (x10 ³ USD)	81	85	79
Condenser Cost (x10 ³ USD)	76	79	75

ID: Internal Diameter; HTA: Heat Transfer Area

As shown on Table 11 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 11, 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. These parameters 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.

The rough costing of purchase and installation of the extractive column, along with its heat transfer equipment, was done. This analysis was also made for the other studies exposed in Table 11. Table 12 shows the general parameters of the costing analysis.

Using the information of previous studies (Xu and Wang, 2006b) and the results of this work, all extractive columns were simulated with the tray sizing option of Aspen Plus, to calculate the diameter. To roughly estimate the cost of shell, trays, auxiliaries purchase and installation, general correlations were used (Peters *et al.*, 2003). For the condenser and reboiler cost, a simulation to find the heat transfer area, was performed. Using Peters *et al.* (2003) graphs the cost of the heat transfer equipment of the extractive column was estimated. Table 13 shows the results.

V. FOR FURTHER INVESTIGATION

In this work Aspen Plus was used to analyze and define a technical and economical suitable entrainer for THF dehydration by extractive distillation. In order to improve these results, the ternary THF-Water-Glycerol VLE, is recommended to be experimentally determined.

On the other hand BASF has recently reported the use of ionic liquids as entrainers for this separation. This new technology has a variety of economical benefits that can be compared to the results of this investigation. It is said that these entrainers break the azeotropes efficiently and would require less equipment and less energy consumption (BASF, 2008). For further analysis these type of substances should be included, emphasizing on the dissociative properties of these substances

(Johnson, 2007), along with their physical properties (especially viscosity) and thermodynamic behaviour (Zhang *et al.*, 2007 and Ge *et al.*, 2008). In this case a rigorous costing study should be made, to compare the installation and operative costs needed to dehydrate THF.

VI. CONCLUSIONS

A better entrainer for the THF dehydration with extractive distillation was found, developing an appropriate methodology of entrainer selection. The sensitivity analysis gave the most suitable conditions to perform the extractive distillation process with the selected entrainer. The simulation results reveal coherent temperature, mole flow and composition profiles. The purity restriction is achieved, with the minimum energy consumption (compared to previous investigations). Aspen Plus is a useful tool for the analysis and design of extractive distillation processes, being suitable not only for the simulation performance itself, but to the entrainer selection method.

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