

# Investigation of Tetrahydrofuran Removal Technology from Process Wastewater

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## Abstract

The work is motivated by an industrial problem, which is tetrahydrofuran removal from pharmaceutical process wastewater with extractive distillation. The goal of the research is to rigorously model and optimize this operation in professional flowsheet simulator environment based on adequate and consistent vapour-liquid equilibrium data. The number of minimal theoretical plates of distillation columns, binary mixture feed stage, solvent feed stage location, optimal reflux ratios and Total Annual Cost (TAC) are determined. Dimethyl sulfoxide (DMSO) is used as extractive agent.

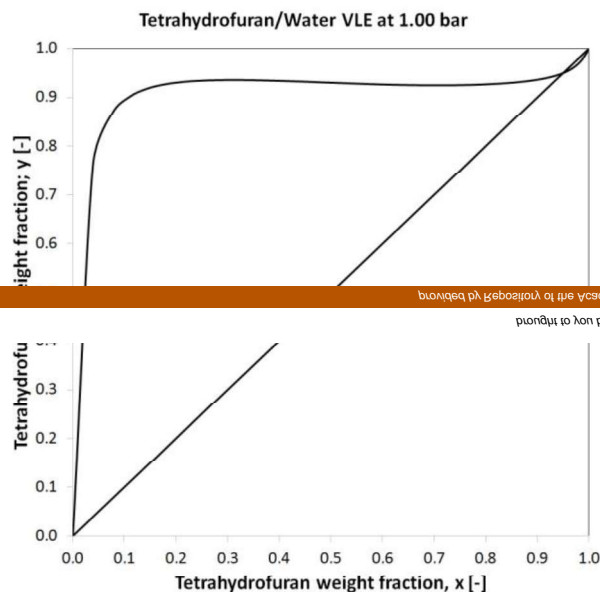
Considering the results, it can be concluded that, the extractive distillation process is suitable for separation tetrahydrofuran and water in 99.9 weight percent (m/m%) purity of water and 99.5 m/m% tetrahydrofuran.

## Keywords

Process wastewater; tetrahydrofuran removal; extractive distillation, flowsheet environment

## INTRODUCTION

Tetrahydrofuran (THF) forms heterogeneous azeotropic mixture with water, which means separation problem. THF content above 93.3 weight% can not be achieved with conventional distillation techniques (Marsden, 1954). The vapour-liquid equilibrium of IPA-Water binary mixture can be seen in Figure 1.



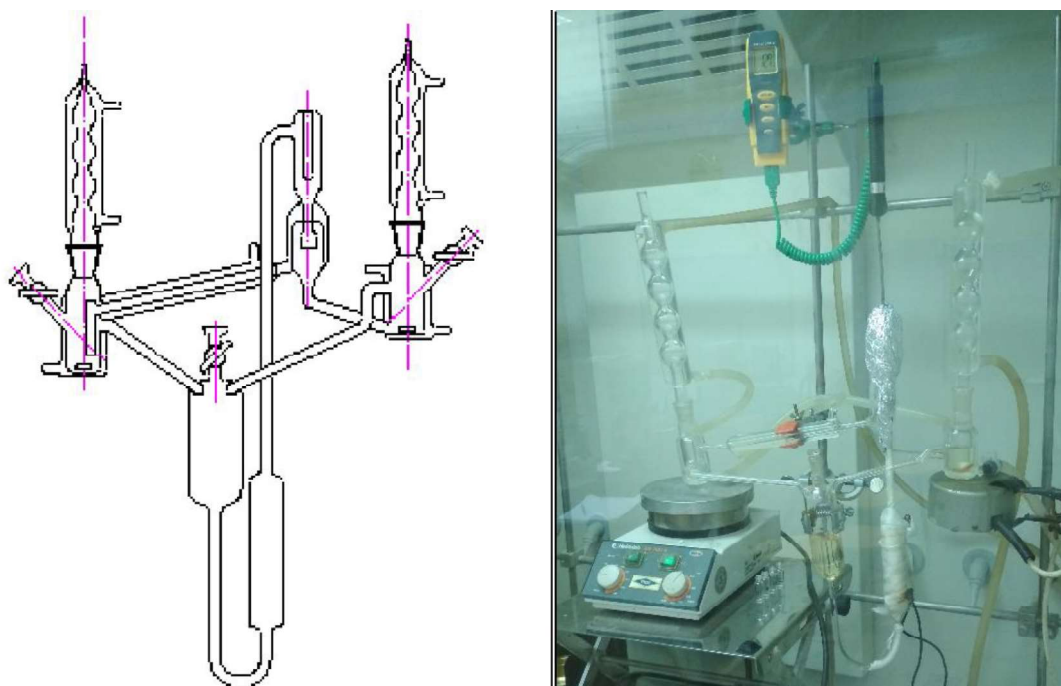
**Figure 1.** Vapour-liquid equilibrium of THF-Water mixture

It can be mentioned, extractive distillation is capable for separation of tetrahydrofuran-water mixture (Xu and Wang, 2006; Zhang et al., 2014; Deorukhkar et al., 2016; Ghuge et al., 2017). This technique has been widespread in the chemical and environmental industries, but it is not economical in many cases in the reason of its high operation cost (Toth et al., 2011; Toth and Mizsey, 2015; Andre et al., 2018).

## MATERIAL AND METHODS

The aim of this study is to remove of tetrahydrofuran from process wastewater (PWW) with extractive distillation in professional flowsheet environment. Consistent vapour-liquid equilibrium (VLE) data is essential for computer simulation, therefore laboratory experiments are required.

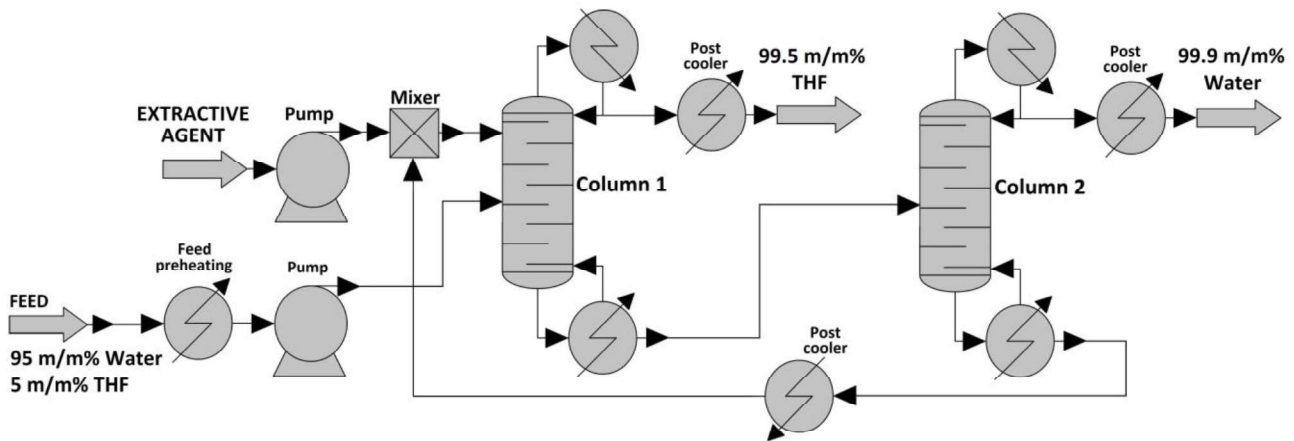
The determination of the VLE measurements of the THF-water binary system are performed by using a modified Gillespie still designed by Manczinger (Manczinger and Tettamanti, 1966) with minor subsequent modifications as shown in Figure 2 (Havasi et al., 2016).



**Figure 2.** Equilibrium apparatus

The tetrahydrofuran concentration is measured with Shimadzu GC2010Plus+AOC-20 autosampler gas chromatograph with a CP-SIL-5CB column connected to a flame ionization detector, EGB HS 600 headspace apparatus is used for sample preparation. The water content is measured with Hanna HI 904 coulometric Karl Fischer titrator (Toth et al., 2015; Toth et al., 2016; Haaz and Toth, 2018).

PWW from pharmaceutical industry has to be separated with the following initial composition: 5 m/m% THF and 95 m/m% Water. The product purity is min. 99.5 m/m% in both cases and 800 kg/h PWW must be treated. The ChemCAD flowsheet of extractive distillation can be seen in Figure 3.



**Figure 3.** Flowsheet of tetrahydrofuran-water separation with extractive distillation

The first column is the extractive column, where the heterogeneous azeotropic mixture can be separated with dimethyl sulfoxide as entrainer. The second column treats the water-dimethyl sulfoxide mixture, the entrainer can be recycled and mixed into the feed stream. The optimal reflux ratio, the mass- and bottom flow rates, heating and cooling requirements, number of theoretical plates ( $N$ ) and feed plate have to be optimized.

## RESULTS AND DISCUSSION

Table 1 introduces the measured vapour-liquid equilibrium data of THF-Water mixture.

**Table 1.** VLE data of tetrahydrofuran-water binary mixture (x: liquid, y: vapour)

T [°C]	p [Pa]	x [-]	y [-]	T [°C]	p [Pa]	x [-]	y [-]
72.98	103.2	0.02	0.6521	63.81	103.2	0.65	0.7764
66.48	103.2	0.04	0.7380	63.68	103.2	0.70	0.7831
65.56	103.2	0.06	0.7514	63.59	103.2	0.75	0.7914
65.31	103.2	0.08	0.7561	63.52	103.2	0.80	0.8083
64.92	103.2	0.10	0.7586	63.51	103.2	0.82	0.8173
64.68	103.2	0.15	0.7617	63.55	103.2	0.84	0.8261
64.31	103.2	0.20	0.7624	63.62	103.2	0.86	0.8367
64.28	103.2	0.25	0.7628	63.71	103.2	0.88	0.8497
64.25	103.2	0.30	0.7634	63.85	103.2	0.90	0.8634
64.23	103.2	0.35	0.7638	64.03	103.2	0.92	0.8835
64.21	103.2	0.40	0.7642	64.27	103.2	0.94	0.9045
64.18	103.2	0.45	0.7647	64.59	103.2	0.96	0.9235
64.14	103.2	0.50	0.7656	65.05	103.2	0.98	0.9614
64.04	103.2	0.55	0.7682	65.37	103.2	0.99	0.9813
63.92	103.2	0.60	0.7719				

The thermodynamic consistency test for THF-Water data is performed according to Herrington's area test (Herrington, 1947; Havasi et al., 2016; Havasi, 2018) for isobaric data.  $D$  and  $J$  values are calculated according to following equations.

$$\gamma_i = \frac{y_i \cdot p}{x_i \cdot p_i^0} \quad (1)$$

$$D = 100 \times \left| \frac{\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2) dx_1}{\int_{x_1=0}^{x_1=1} |\ln(\gamma_1/\gamma_2)| dx_1} \right| \quad (2)$$

$$J = 150 \times \frac{|\Delta T_{\max}|}{T_{\min}} \quad (3)$$

$$D - J \leq 10\% \quad (4)$$

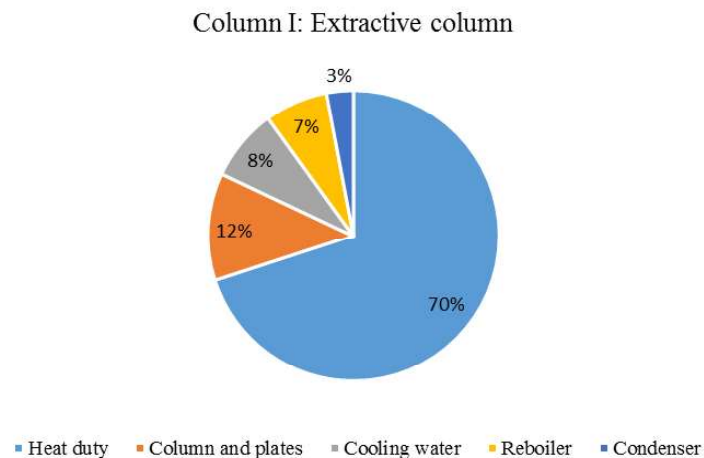
It can be concluded, D-J is 9.8, therefore the measured data is capable for application in flowsheet environment.

The optimized results of simulations with extractive distillation process is listed in Table 2.

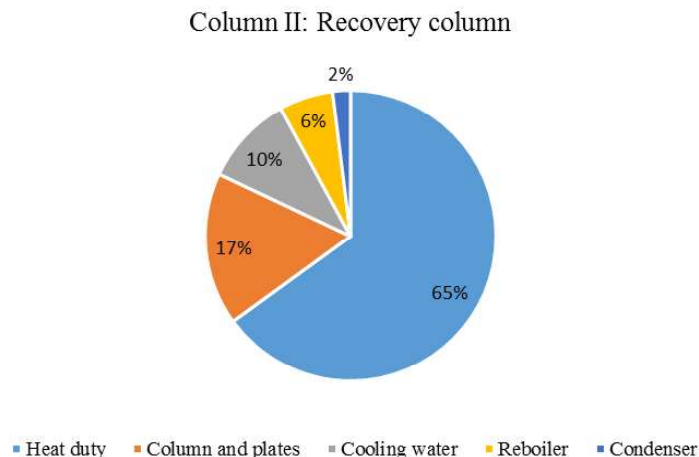
**Table 2.** Optimized results of tetrahydrofuran-water separation

	Extractive column	Recovery column
N [-]	15	20
Feed stage (PWW)	7	8
Feed stage (DMSO)	2	-
Reflux ratio [-]	3	1
THF [m/m%]	99.5	0.05
D Water [m/m%]	0.3	99.9
DMSO [m/m%]	0.2	0.05

The Total Annual Cost (TAC) is also determined, using Douglas-correlations (Douglas, 1988). Figure 4 and Figure 5 show the distribution of TAC in both column cases.



**Figure 4.** Distribution of Total Annual Cost of Extractive column (C1)



**Figure 5.** Distribution of Total Annual Cost of Recovery column (C2)

It can be concluded, heat duty/cost of distillation has the largest part of TAC.

## SUMMARY

The extractive distillation is investigated in professional flowsheet environment. It can be concluded tetrahydrofuran-water mixture can be separated into pure components with this operation. The goal composition, which is min. 99.5 m/m% in both product case can be reached.

## ACKNOWLEDGEMENT

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