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# SOLVENT RECOVERY FROM A MULTICOMPONENT MIXTURE BY BATCH EXTRACTIVE DISTILLATION AND HYBRID PROCESS

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## Abstract

The performance of the basic and a modified operational policy of batch extractive distillation (BED) and the hybrid process (HP; absorption+distillation) for the recovery of tetrahydrofuran (THF) from a five-component industrial waste solvent mixture were investigated with laboratory experiments and rigorous simulations. The components (methanol, THF, acetonitrile, water, pyridine) of the mixture form seven azeotropes. The prescribed separation task (production of aqueous THF with limited content of organic pollutants) was not feasible with batch rectification, but we were able to produce THF of desired quality by BED and HP using water as entrainer. The highest recovery and production rate were achieved with the HP, while the least efficient process was the basic policy of BED.

**Keywords**: batch distillation, extractive distillation, hybrid process, azeotropes

## 1. Introduction

For the separation of components forming azeotropes, special distillation methods must be applied. One of these methods is the extractive distillation, where the separation is made possible by addition of an entrainer, which is not necessarily a further component. Batch extractive distillation (BED) unifies the advantages of batch and extractive distillation[1]. By the modified version of BED, there is no external reflux[2]. This process is called hybrid process (HP) as it can be considered as a hybrid of distillation and absorption. By the hybrid process, contrary to BED, the entrainer is highly sub-cooled liquid and it is always fed into the top plate of the column. Comparing the performance of BED and HP in the separation of acetone-methanol and ethanol-water mixtures using water and ethylene glycol as entrainers, respectively, Kotai et al.[3] concluded that BED is more flexible than the HP, but HP can be competitive if there is no strict requirement for the separation of the light component and the entrainer.

The recovery of THF from a waste solvent mixture containing four organic components (methanol (A): 1.5 mass%, THF (B): 86%, acetonitrile (C): 9%, pyridine (E): 2%) and water (D, 1.5%) had to be solved. The THF should not contain more than 0.5% of the other organic components. The goal of this paper is to present and evaluate laboratory experiments of the two policies of BED and HP, and to compare their performance (recovery, energy and entrainer consumption, water content of the product).

## 2. Vapour-liquid equilibrium

### *2.1 The VLE data of the components*

For the calculation of vapour-liquid equilibrium, the UNIQUAC model was used. In the case of mixture B-C, which is crucial for the appropriate description of the equilibrium, the literature was contradictive: Gmehling and Bölts[4] gives the composition of an azeotrope, while the experimental data published by Darwish and Abdallah[5] indicate that the components do not form azeotrope. We used parameters regressed from aforementioned experimental data to be able to describe the experimental results. Table 1 shows the boiling points and compositions of the components and the seven azeotropes.

### *2.2. The effect of entrainers on the relative volatilities*

The A-B, A-B-C, and B-C azeotropes disturb the production of THF. One possible method to break these azeotropes is extractive distillation. The effect of the addition of water (D) and E – both of which are already present in the mixture and have high boiling points – on the relative volatilities of A-B and B-C mixtures of azeotropic compositions were investigated by VLE calculations. Both entrainers can be subsequently easily separated from the THF produced: the water by drying, E by distillation, respectively. Plotting the relative volatilities $\alpha_{AB}$ and $\alpha_{BC}$ (Fig. 1) against the added amount of entrainer, we can conclude that both solvents reverse the volatility order in the mixture A-B (rendering B more volatile) and increase the volatility of B in the mixture B-C. In the first case water, in the latter one E proved to be more efficient. However, using water is more practical, as it has a lower molar volume, it is more available, cheaper, and non-toxic. Thus, further investigations were only performed for water.

**Table 1.** The boiling point and compositions of pure components and azeotropes

| Component(s) | $T_{bp}$ (°C) | Composition (mass%) | | | | |
|---|---|---|---|---|---|---|
| | | A | B | C | D | E |
| A-B | 59.5 | 25.9 | 74.1 | - | - | - |
| A-C | 63.6 | 77.4 | - | 22.6 | - | - |
| B-C-D | 63.7 | - | 87.8 | 7.1 | 5.1 | - |
| B-D | 63.89 | - | 94.7 | - | 5.3 | - |
| A | 64.7 | 100 | - | - | - | - |
| B-C | 65.8 | - | 88.4 | 11.6 | - | - |
| B | 65.97 | - | 100 | - | - | - |
| C-D | 76.5 | - | - | 84.2 | 15.8 | - |
| C | 81.6 | - | - | 100 | - | - |
| D-E | 92.6 | - | - | - | 43 | 57 |
| D | 100 | - | - | - | 100 | - |
| E | 115.2 | - | - | - | - | 100 |

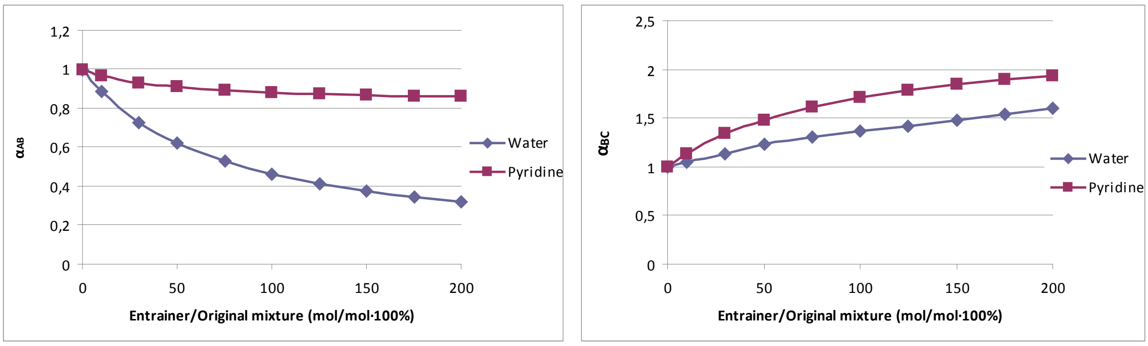

**Figure 1.** The effect of the entrainer on the relative volatilities of A-B and B-C mixtures

## 3. The operation modes studied

For the recovery of THF, the basic and a modified policy of BED, as well as the HP were investigated. The operation steps of the basic, conventional policy of BED are the following: after the start-up (Step 1) the purification step (Step 2) is started, in which the water feeding extracts components A and C out of the top product under infinite reflux ratio (R). Step 3 is the production of aqueous THF under finite R and water feeding. The other organic components are removed from the reboiler in Step 4, without water feeding. Possible termination criteria of the respective steps are:

1. Reaching steady-state operation (constant temperatures).
2. The sum of the concentrations of A and C at the top of the column falls below the prescribed value.
3. The concentration of organic impurities (A and C) in the distillate reaches the maximal allowed value.
4. The organic content of the distillate falls below a given value (the top temperature is close to 100 °C).

By the modified operation policy, water feeding is already started during the start-up. In this way, it is possible to extract impurities before their concentration reaches the steady-state value, and to decrease the duration of the process. In this case, Step 1 is the heating-up without water feeding, Step 2 is the heating-up with water feeding. Step 1 is terminated when the vapour reaches the water feed stage, while Step 2 finishes when it reaches the top of the column.

With HP it is possible to decrease the duration of the process further and to extract the organic impurities more efficiently. In this case, as there was no strict limit prescribed for the water content of the product, HP is a suitable alternative to BED. If water feeding is already started – similarly to the modified policy of BED – during start-up, then Steps 1, 2 and 4 are identical with those of the modified policy of BED. Step 3, the production of aqueous THF with absorption (R=0) is significantly shorter than the production steps of the BED processes. The termination criteria are the same as those for the modified policy of BED.

## 4. Experimental part

*4.1 Preliminary simulations*

Before starting the experiments, preliminary calculations were done with CC-BATCH dynamic simulator for BD, basic BED and basic HP. On the basis of the results, the value of the main operational parameters (R, flow rate of water) was selected for the experiments. We stated that the separation is feasible with the extractive distillation methods.

*4.2 The experimental apparatus*

Experiments were carried out in the laboratory distillation column (Fig. 2). The still – a round bottom flask of 2 $dm^3$ – can be heated with a heating basket. The glass column has a diameter of 5 cm, and is filled with PROPAK unstructured packing (0,16 in) in the height of 153 cm. The column is equipped with four thermometer stubs, one of which was used for feeding water into the column. Temperatures were measured in five different locations (top, still, 3 different heights in the column). The analysis was performed by gas chromatography (CHROMPAK with FFAB CB25 mx column).

*4.3 The experimental results*

Four experiments were performed. The approximate composition of the charge was the following: 1.5 mass% A, 86 % B, 9 % C, 1.5 % D, 2 % E. The amount of charge (1 $dm^3$) and the reflux ratio (5) were the same, with the exception of HP. The temperature of the entrainer was approximately 60 °C in the BED experiments, and 18 °C in the HP experiment, respectively. The most important data of the experiments are presented in Table 2.

A conventional batch distillation (reference) experiment was carried out to prove that the separation is infeasible with this method. Acceptable product was not obtained at all.

To investigate the applicability of BED, its basic policy was experimentally realized. It was proven that it is possible to produce THF of the prescribed quality with acceptable recovery (70.1 %) under moderate R and specific water consumption (SWC).

In the third experiment (BED modified policy) water feeding was already started during start-up. The concentration of organic impurities in the product was well below the limiting value, while recovery was higher (80.6 %) than that of the second experiment. Specific water consumption was smaller by the modified policy.

The fourth experiment was carried out in order to study the HP. During the production the flow rate of water was much higher than that for the BED. We were able to produce THF with very good recovery (92.0 %), with slightly higher water consumption. The water content of the product was also higher (7 %), which could mean higher drying costs. It was possible to considerably decrease the duration of the separation process (from 310 to 168 minutes). It must be still mentioned, that under the given experimental conditions it was only possible to feed the water through the first temperature stub, reducing the number of theoretical stages with cca 20 %

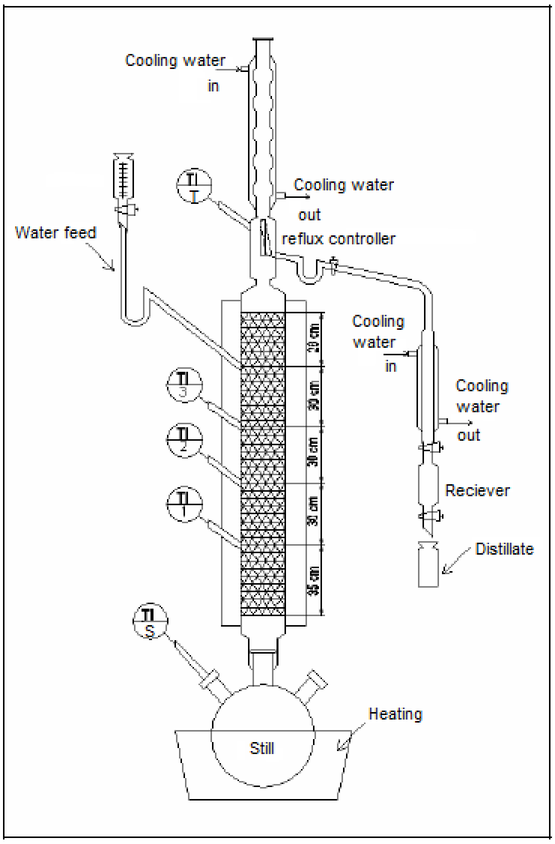

**Figure 2.** The sketch of the laboratory distillation column (BED and HP)

**Table 2.** The most important data of the experiments

| Method | Time (min) | Charge (g) | Product composition (mass%) | | | Recovery (%) | SWC (kg water/kg product) | Water feeding (dm$^3$/h) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | A+C+E | B | D | | | Step 2 | Step 3 |
| BD | 535 | 847.1 | 2.88 | 91.96 | 5.15 | - | - | - | - |
| BED basic | 363 | 875.2 | 0.33 | 94 | 5.67 | 70.1 | 2.23 | 0.46 | 0.37 |
| BED modified | 310 | 878.4 | 0.06 | 93.66 | 6.11 | 80.6 | 1.96 | 0.44 | 0.39 |
| HP | 168 | 657.2 | 0.21 | 92.55 | 7.01 | 92 | 2.32 | 0.42 | 0.93 |

## 5. Simulation results

### *5.1 Simulation method*

Posterior calculations were performed with the CC-DCOLUMN dynamic professional flowsheet simulator. The following simplifying assumptions were used: theoretical plates, constant liquid hold-up on the plates, negligible vapour hold-up, negligible pressure drop, perfect mixing on the plates and in the vessels. The model of the HP is presented in Figure 3. The encircled numbers identify the respective unit operations. The model consists of the column (SCDS, 1), the condenser (HEAT EXCHANGER, 8), four DYNAMIC VESSELs (2: still, 3-5: receivers), two MIXERs (10, 11), two TIME SWITCHes (6, 7) and a DIVIDER (9), by which reflux ratio can be set. Stream No. 19 is the water feeding. In the case of BED, reflux and water streams are fed separately into the column.

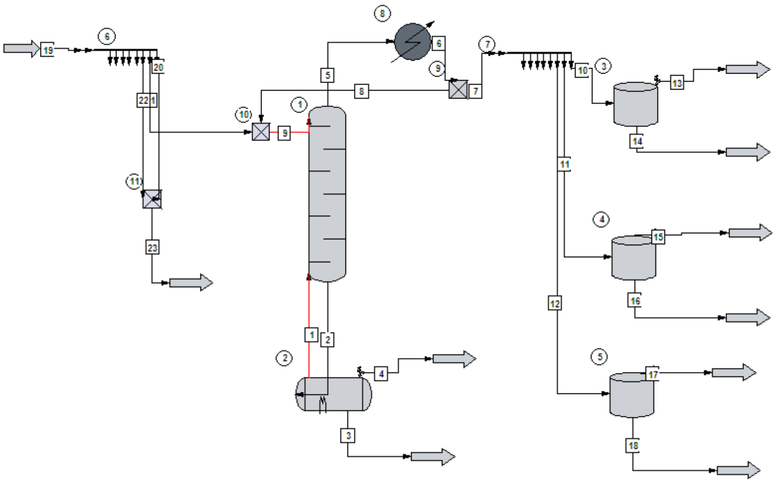

**Figure 3.** The CC-DCOLUMN model of hybrid process.

*5.2 Posterior simulation results*

The posterior simulation of BED and HP experiments were performed on the basis of the distillate's measured mass flow rate. The theoretical plate number (excluding the still) was estimated as 22 (BED) and 17 (HP), respectively. The description of the experiments was made more difficult by several factors: the limited accuracy of the description of VLE conditions, the varying water flow rate, and the uncertainty in the number of theoretical plates.

The calculated recoveries (Table 4) are in acceptable agreement with the experimental ones. The total organic impurity content is higher than the measured value in the case of BED experiments, allowing a safe estimation of the experimental quality. However, in the case of HP, the measured impurity concentration (0.21) was found to be higher. Figure 4 shows the evolution of the measured and calculated distillate compositions in the case of HP.

**Table 4.** The results of posterior simulations

| | Recovery (%) | Organic impurities in the THF (mass%) | Specific energy consumption (MJ/ kg product) |
|---|---|---|---|
| BED basic | 69.4 | 0.73 | 8.66 |
| BED modified | 79.4 | 0.65 | 5.85 |
| HP | 89.1 | 0.09 | 2.61 |

*5.3 The effect of operational parameters*

The effect of operational parameters on the recovery, specific energy (SEC) and water consumption (SWC) were investigated for the modified policy of BED and HP. The parameters studied were: the position of feed stage (f), the reflux ratio (only in the case of BED), the water flow rate during heating-up ($W_1$) and production ($W_2$). The basic value of the parameters was the experimental ones. The consumptions are calculated until the end of the main cut.

By BED, the maximal allowed concentration of organic impurities was 0.65 mass% that assuredly corresponds to an acceptable experimental purity. The results using the base parameters: recovery is 72.8 %, SEC=5.1 MJ/kg, SWC=2.7 kg/kg. The position of feed plate has the greatest effect: if water was fed to the first, the recovery would become 90.9 %. R has an optimal vale (4), however its influence is slight. Recovery increases with both flow rates, but its growth is relatively small compared to that of the SWC. We suggested modifications in the values of operational parameters. For f=1 and R=4, recovery increases considerably (to 96.1 %). At the same time, both specific consumptions are reduced: SEC=3.7 MJ/kg, SWC=1.9 kg/kg. The water content of the product (6.8 %), however, is almost as high as in the case of HP. Since under the given experimental conditions, it is not possible to feed the water higher than plate 7, we can state that the experimental parameters were well chosen.

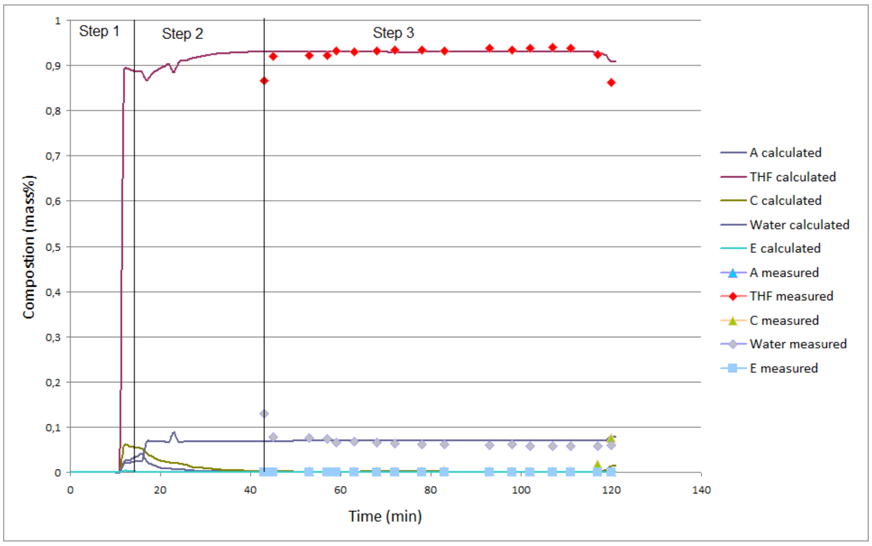

**Figure 4.** Evolution of the measured and calculated distillate composition (HP)

In the case of HP, the total concentration of organic impurities was limited in 0.5 mass%. The results of the base case: recovery is 98.1 %, SEC=2.0 MJ/kg, SWC=2.8 kg/kg. With the increase of the flow rates, the specific consumptions increase, while the change in recovery is very small. At the expense of a small decrease in recovery, it is possible to decrease the specific consumptions. We can conclude that the experimental parameters were well chosen, only a slight decrease of $W_1$ would be advisable.

### *5.4 Comparison of BED and HP*

Comparing the modified policy of BED (which proved to be the better of the two BED policies) and HP, using the modified operational parameters, we found that the recoveries of the two methods are similar. At the expense of higher specific water consumption and the higher water content of the product, HP is capable of considerably faster production, and thus smaller specific energy consumption.

## 6. Conclusions

The performance of the basic and a modified operational policy of batch extractive distillation (BED) and the hybrid process (HP) for the recovery of THF from a five-component industrial waste solvent mixture were investigated with laboratory experiments and rigorous simulations. The components (methanol, THF, acetonitrile, water, pyridine) of the mixture form seven azeotropes. The effect of using water or pyridine as entrainer was investigated, and it was stated that though both entrainers influence the relative volatility favourably, water is more practical to use. Experiments were performed on a laboratory packed column. The prescribed separation task was not feasible with batch rectification, but we were able to produce THF of desired quality by BED and HP using water as entrainer. The highest recovery and production rate were achieved with the HP, while the least efficient process was the basic policy of BED. However, the water content of the product was also the highest in the case of HP. The operational parameters of the experiments were determined by preliminary rigorous simulation. The results of the posterior simulations verified that experimental parameters were well chosen.

## Acknowledgements

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