INDUSTRIAL APPLICATION OF A NEW BATCH EXTRACTIVE DISTILLATION OPERATIONAL POLICY

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From a waste solvent mixture of acetone-methanol-ethanol-water of a pharmaceutical plant acetone is recovered by batch extractive distillation using water as solvent. Besides the former, basic operational policy a new policy resulting in considerable saving of energy and solvent is also applied and studied. Both laboratory and industrial experimental results are compared with those of the rigorous simulation.

KEYWORDS: extractive distillation, batch rectifier, industrial experiments, rigorous simulation

INTRODUCTION

The batch extractive distillation (BED) is an efficient method for the separation of azeotropic and low relative volatility (low α) mixtures. The basic BED operational policy for the separation of minimum azeotropes was suggested and analysed in a batch rectifier (BR) by Yatim et al. (1993) and Lang et al. (1994) for the mixture acetone (A) − methanol (M) + water (W, solvent). The main steps of the process:

1. Heating-up under infinite reflux ratio (R = ∞) without solvent feeding (F = 0).
2. Purification of the distillate under R = ∞ and continuous solvent feeding (F > 0) until $x_{D,A}$ takes its max. value.
3. Production of A under continuous solvent feeding (R < ∞, F > 0)
4. Separation M/W (R < ∞, F = 0)

Several BED operational policies were studied by Lelkes et al. (1998). Among others it was shown that the Step 2 can be shortened (e.g. by ending Step 2 when the prescribed product purity is reached, named hereafter basic operational policy). The same conclusion was drawn by Low and Sorensen (2002). They studied and optimised the separation of the above mixture in a Middle Vessel Column (MVC) and stated that the batch rectifier was very close to the optimal operation of the MVC. During the last decade the performance of the BED in MVC was studied by several teams by simulation (e.g. Safrit et al. 1995, Warter et al. 1999, Hilmen 2000) and by laboratory experiments (Cui et al. 2003, Warter et al. 2004). In the MVC experiments the continuous withdrawal of the bottoms (heavy solvent), which would be the main advantage of the MVC over the BR, was not performed.

Although the BED was already successfully applied for the separation of the above mixture in industrial size in 1995 by Manczinger et al. in the Chinoin Pharmaceutical

Works (actually Sanofi-Aventis Hungary) industrial application(s) of the BED is not known for the researchers.

In 2005 the BED was again successfully applied for the separation of a mixture acetone-methanol-ethanol(E)-water in industrial size. A new operational policy was applied. The functions of the first two steps of the basic operational policy were already performed during the heating-up of the column. The solvent feeding was already started when the charge reached its boiling point in the reboiler. In this case there is no steady state operation at the end of the heating-up.

The aims of our paper are to present the (experimental and simulation) results of the industrial application of this modified policy and their comparison with those of the basic operational policy.

METHOD OF RIGOROUS SIMULATION

The rigorous simulation of both the laboratory experiments and the experimental productions were performed with the CHEMCAD 5.5 professional flow-sheet simulator package. The simplifying assumptions:

- theoretical trays,
- negligible vapour hold-up,
- constant volume of liquid hold-up (excepted the dry start-up and the reboiler).

For all calculations the simultaneous correction method was applied. For describing VLE the UNIQUAC model was applied with the parameters taken from the database of the program.

For the simulation of laboratory experiments (made by the basic operational policy) the program CCBATCH (BATCHCOLUMN module) was applied. For Step 1 ($R = \infty$, $F = 0$) only the final steady-state was simulated. In the preliminary simulation (before the experiments) for each step the heat duty of the reboiler (Q) was specified. In the subsequent simulation for the steps with distillate withdrawal the mass flow rate of the distillate (m_D) was fixed instead of Q. The number of theoretical stages of the column was guessed on the basis of the comparison of experimental and simulation results. The hold-up of the column was estimated on the basis of $R = \infty$ experiments with different heating powers.

The subsequent simulation of the experimental productions was done with the program CCDCOLUMN. The column itself was modelled with the module DYNCOLUMN, the reboiler and the distillate tank with the DYNAMIC VESSEL, respectively. In this case it was not possible to directly specify m_D. The value of Q was estimated on the basis of the approximate simulation of the acetone production step with CCBATCH.

LABORATORY EXPERIMENTS

A simple packed laboratory distillation column (Figure 1) of internal diameter of 5 cm was transformed for the purpose of BED experiments. The diameter of PROPAK random packing: 0.16 inch (cca. 0.4 cm). The height of the packed section: 1.6 m. The volume
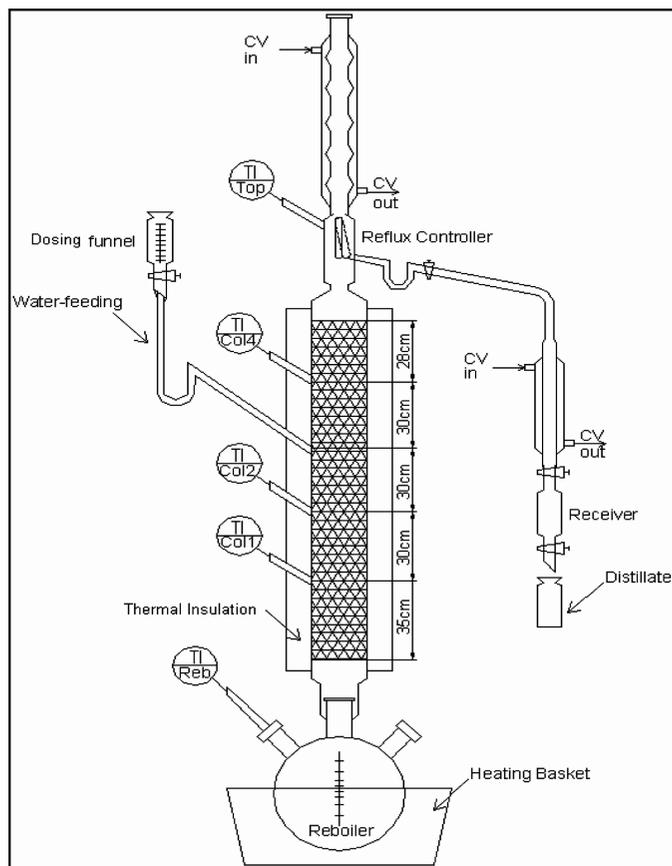
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Figure 1. The sketch of the laboratory BED column

of the reboiler, which is heated by an electrical heating basket, is 2 dm^3. The maximal nominal heating power is 400 Watt (3 different electric heating power can be set.). The continuous water-feeding is insured from a dosing funnel through a thermometer stump to the column. (One of the four thermometers (TI3) of the original BD column was removed for the BED experiments.) The temperature was measured in the still pot, in the column at 3 different heights (two of them below, one above the water-feeding, respectively) and at the top. The reflux ratio can be set by the aid of a timer and an electromagnet. The still pot is calibrated and so the volume of liquid in the boiler (and the volumetric hold-up of the column) can be measured. The analysis of the organic

compounds is performed by gas-chromatograph (CHROMPACK, column: FFAP CB; 25 m × 0,53 mm). The water content is determined by Karl-Fischer method.

Altogether 6 laboratory experiments were performed: one reference (batch distillation (BD)) and five BED experiments. Before them we experimentally studied the net heat duty, the hold-up (between 0.2 and 0.3 dm^3 depending on the heating power) and the number of theoretical plates of the column (about 10, excluding the condenser and reboiler), as well. The parameters of the experiments were selected on the basis of preliminary rigorous simulation calculations made with the CHEMCAD professional flowsheet simulator (BATCHCOLUMN module). We present the results of one experiment made by the basic operational policy of the BED.

Product (A) purity requirements: the max. concentration of the pollutants: 0.5 mass % M, 2% E, 0.8% W
The data of the operational parameters:
Volume of the charge (feed): 1.2 dm^3
Charge composition: 44.2 mass % A, 2.13% M, 3.62% E, 50.5% W
Reflux ratio: in Steps 1 and 2: ∞   in Step 3: 5
Av. flow rate of water-feeding, dm^3/h: in Step 2: 0.426   in Step 3: 0.429
Temperature of water-feeding: cca. 60 °C
Duration of Step 2: 60 min
Nominal heating power: in Step 1 and for 15 min in Step 2: 267 W   Later: 400 W

The evolution of the distillate composition (given by the composition of the fractions of 25 or 50 cm^3) is shown in Figure 2.
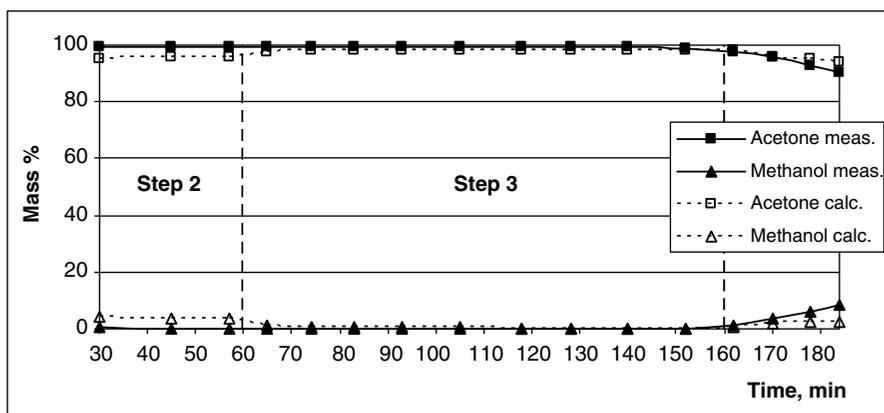

Figure 2. The evolution of the distillate composition in a laboratory experiment (basic operational policy)

The methanol concentration decreased below its allowable max. value during Step 2 and further decreased at the beginning of Step 3 and it remained very low for long time.

The average composition of the main cut:

by experiment: 99.00 mass % A, 0.16% M, 0.16% E, 0.68% W.

by simulation: 98.36 mass % A, 0.31% M, 0.07% E, 1.26% W

The recovery of A: by experiment: 76.9%   by simulation: 79.2%

We can conclude that a product whose purity was higher (mainly for M) than the prescribed minimal one was produced with good recovery under moderate reflux ratio and water consumption. Taking into consideration the inaccuracies of the experimental data (e.g. loss of vaporization), analysis and simulation we can tell that experimental and simulation results showed acceptable agreement.

EXPERIMENTAL PRODUCTION IN INDUSTRIAL SIZE

After the favourable results of the laboratory experiments and simulation the BED was applied for the recovery of acetone in an industrial column. The main data of this column: number of bubble cap plates: 50, internal diameter: 1.25 m, volume of the reboiler: 25 m^3, surface of the reboiler: 50 m^2, surface of the condenser: 100 m^2.

For heating water steam of 5 bars was applied. The guessed volumetric holdup of the condenser is 0.5 m^3, that of the column: 1.5 m^3. The water applied as solvent was not preheated. The top and bottom temperatures are taken. (The method of analysis and purity requirements are the same as for the laboratory experiments.) Several batches were processed. At the beginning the basic operational policy of the BED was applied. On the basis of the first experimental results (the water content was very close to its max. value while the methanol content was far below it) the water-feeding was introduced to a lower plate, the reflux ratio was slightly increased, the flow rate of water was decreased during the acetone production step. By the basic operational policy several hours were necessary after the end of heating-up of the column (Step 1) for the purification of distillate from the methanol (Step 2) to the specified extent. Therefore water-feeding was started earlier when the liquid begun to boil in the reboiler (indicated by the increase of temperature). The results of an experimental production performed by this modified operational policy will be shown.

Since the top temperature does not indicate unambiguously the achievement of the prescribed quality of the distillate (Figure 3c) because of the time requirement of the analysis the distillate withdrawal was started only one hour after the end (indicated by the constancy of the reflux flow rate) of the heating-up (combined with the simultaneous extraction of the methanol by water-feeding) of the column.

The flow rate of water-feeding was considerably decreased at the end of heating-up. It was increased twice near the end of production (main-cut) when the methanol content of the distillate begun to rise.
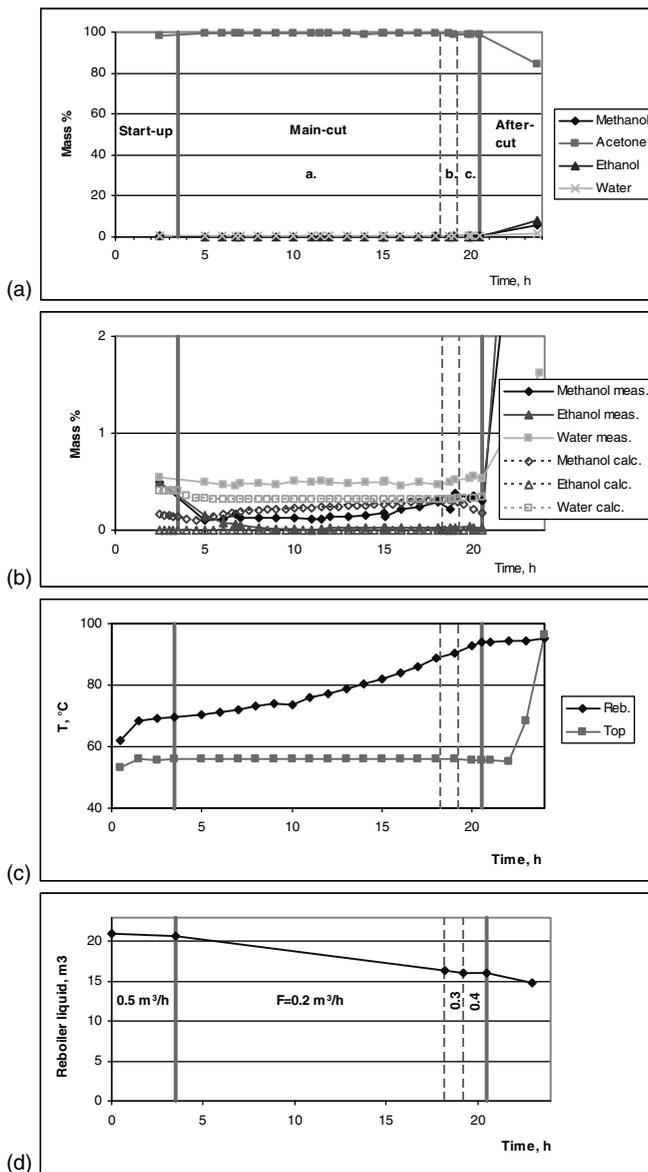
Figure 3. Results of the experimental production (modified policy). Evolution of (a) distillate composition (b) concentration of pollutants in the distillate (c) top and bottom temperatures (d) liquid volume in the reboiler

The value of the most important operational parameters:

Volume of the charge: 21 m^3 Solvent-feeding plate: 21th (from the top)
Charge composition: 45.59 mass% A, 1.13% M, 1.90% E, 51.38% W
Reflux ratio: Heating-up: ∞   Production: 7
Flow rate of water-feeding, m^3/h:

Heating-up: 0.5 ($\Delta t = 3.5$ h)

Production: 0.2 ($\Delta t = 14.75$ h), 0.3 ($\Delta t = 1$ h),   0.4 ($\Delta t = 1.25$ h)

The evolution of the distillate composition is shown in Figures 3a and 3b, that of the temperatures in Figure 3c and the liquid volume in the reboiler in Figure 3d.

The methanol content of the distillate decreased (just) below 0.5% already during the heating-up (at t = 2.5 h) and then further decreased. Both the methanol and acetone content remained much below its maximal allowable value during the whole production. The calculated water and ethanol concentrations of the distillate are somewhat higher; those of the methanol are somewhat lower than the experimental ones.

The forthcoming deterioration of the distillate quality is not predicted by the variation of top temperature at the end of the production step. After the stopping of water-feeding (at the beginning of the after-cut) the top temperature slightly decreased for 1.5 hour.

The liquid volume in the reboiler (Figure 3d) was never higher than the volume of the charge. During the heating-up the formation of the liquid holdup of the column and condenser compensated the effect of water-feeding. During the production of the main cut the liquid volume in the reboiler steadily decreased.

The average composition of the main cut:

by experiment: 99.27 mass %A, 0.17% M, 0.05% E, 0.51% W.
by simulation: 99.46 mass %A, 0.22% M, 0.00% E, 0.32% W.

The recovery of A:

by experiment: 77.5%   by simulation: 80.3%

We can conclude that a product of quality significantly better than the prescribed minimal one was manufactured with good recovery under moderate reflux ratio and water consumption. Experimental and simulation results showed acceptable agreement.

COMPARISON OF THE OPERATIONAL POLICIES

The two different operational policies were studied and compared with each other by simulation, as well. The hold-up of the column, that of the condenser, data of the

charge were taken from the results of experimental production. The heat duty in the reboi-ler: 1 900 MJ/h (on the basis of the simulation of experimental production). The other common input data for the two policies: Number of theoretical plates: 25 (excluding the condenser and reboiler) Water-feeding plate: 11.

First the basic operational policy (I) was studied. The heating-up (from the boiling point of the charge; under $R = \infty$, $F = 0$) was finished after 1.5 h. In Step 2 the methanol was extracted with a water flow rate of 0.5 m^3/h (under $R = \infty$) until all purity require-ments were satisfied. The heat (SQ_I) and water consumptions (SF_I) of these two prepara-tory steps were determined, that is, the amount of heat and solvent, which is necessary before the beginning of the production step by the basic operational policy were calculated.

By the basic operational policy Step 1 has detrimental effect for the A/M separation (Figure 4). The distillate composition tends toward that of the binary A-M azeotrope, $x_{D,M}$ increases and $x_{D,A}$ decreases (not shown). At the end of this step the acetone/methanol (mass) ratio is smaller (37.9) than in the charge, where this ratio (40.3) is much higher than in the azeotrope (7.25). (It must be mentioned that so far in the literature the separation of equimolar (or azeotropic) charge was studied.) In Step 2 very long time is necessary for reaching the prescribed distillate purity (extraction of methanol).

Then by the modified policy (II) we tried to produce prescribed purity distillate (Figure 4) with the same flow rate of water ($F_{II} = F_I$) and heat duty ($Q_{II} = Q_I$). After a slight increase of duration of only 0.17 h $x_{D,M}$ decreases quickly and so the specified
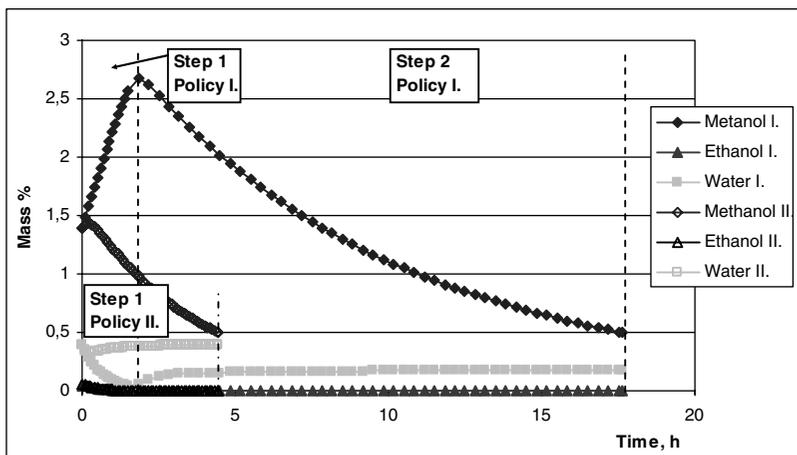

Figure 4. Evolution of the distillate composition before the start of the production by the two policies

distillate purity is reached much more quickly than by Policy I. The water content of the distillate is somewhat higher than by Policy I but it remains much below its allowable maximal value.

We can conclude that before the production prescribed purity distillate can be reached with much smaller solvent and energy consumptions by the modified policy.

CONCLUSION
After rigorous simulation calculations and laboratory experiments a mixture of acetone-methanol-ethanol-water was successfully separated by batch extractive distillation (BED) in industrial size by using water as solvent. Since the step of heating up under infinite reflux ratio without solvent feeding of the basic operational policy had detrimental effect for the acetone/methanol separation in the case of the given composition charge a new operational policy was applied. The solvent feeding was already started when the charge reached its boiling point in the reboiler. This modified policy resulted in significant saving of energy and solvent.

ACKNOWLEDGEMENT

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