A New Batch Extractive Distillation Operational Policy for Methanol Recovery

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The recovery of methanol from a multicomponent aqueous waste solvent mixture was studied. The components form several minimum azeotropes, of which the methanol-THF and methanol-toluene azeotropes limit the recovery of methanol by traditional batch distillation (BD). THF and toluene are removed in the fore-cut, causing a significant loss of methanol.

The addition of water decreases both methanol-THF and methanol-toluene relative volatility, and therefore by feeding water as entrainer, methanol loss can be decreased. A new BED operational policy is suggested, where water feeding is applied only during the heating-up of the column (BED1). Compared to BD, at the end of the heating-up, the concentration of organic pollutants is increased, and that of methanol is significantly decreased in the top of the column. Water feeding can continue during the fore-cut (BED2), but this increases the amount of fore-cut and dilutes the mixture from which methanol is recovered.

Laboratory experiments were performed in a packed column to compare the BD and the two BED operational policies. The highest recovery was obtained by BED1, the lowest one by BD. The preliminary and posterior rigorous dynamic simulation of the experiments was made with a professional dynamic flowsheet simulator. Industrial-size pilot productions of BD and BED1 in a 50 bubble cap tray column also showed a 5% increase in methanol recovery.

1. Introduction

Batch distillation (BD) is often applied for the separation of mixtures with variable quantity or composition, for example, pharmaceutical waste solvent mixtures (Mujtaba, 2004). These mixtures often contain several components forming azeotropes with each other, which renders the recovery of the main component more difficult, or even infeasible. In these cases, special distillation methods should be applied, e.g. extractive distillation. In batch extractive distillation (BED), an entrainer, which is not necessarily a new component, is fed continuously into the column, changing the relative volatilities favourably (Luyben and Chien, 2010).

The usual application of BED is to extract pollutants of moderate concentration from the main component to be recovered. In certain cases, the effect of the entrainer is the contrary, as it reduces the volatility of the main component, which is extracted from beside the pollutants of low concentration forming minimum azeotropes with it. These components can be removed in fore-cuts. The loss of the main component in the fore-cuts can be decreased by BED. However, the high amount of entrainer fed renders the separation of the main component from it more difficult. Thus, the application of BED can be even uneconomical.

The feeding of the entrainer can be started after the start-up of the column, or during the heating-up, as early as the vapour reaches the location of the feed, as suggested by Lang et al. (2006).

The aim of this paper is to present a new batch extractive distillation policy, where the entrainer feeding is only applied during the heating-up of the column, and the entrainer extracts the main component from beside the pollutant components, removed in the fore-cuts. The waste solvent mixture of a pharmaceutical plant contains acetone (A), methanol (B), tetrahydrofuran (C), n-hexane (D), ethanol (E), water (F) and toluene (G), from which methanol is to be recovered in a purity of min. 99.5 mass%. The new BED policy is compared with BD and the traditional policy of BED by laboratory and industrial-size experiments.

2. Vapour-liquid equilibrium conditions

The mixture contains *B* as main component, two organic pollutants in moderate concentration (*C* and *G*), water (*F*), and three organic pollutants (*A*, *D* and *E*) in very low concentration (less than 0.5 mass% together). Though the latter three components, form azeotropes, they do not cause a notable loss of *B*. Therefore, we will focus on the four components with higher concentration, although all the components are included in the simulation. The boiling points of these components and their azeotropes, together with the azeotropic compositions are given in Table 1. The azeotrope *F-G* is heterogeneous.

Table 1: Boiling points and compositions of the four most important components and their azeotropes

Component	T_{bp} (°C)	Composition (mass%)			
		B	C	F	G
B – C	59.5	30.0	70.0	-	-
B – G	63.6	71.5	-	-	28.5
C – F	63.9	-	94.3	5.7	-
B	64.7	100	-	-	-
C	65.97	-	100	-	-
F – G	84.4	-	-	19.7	80.3
F	100.0	-	-	100	-
G	110.6	-	-	-	100

The recovery of *B* is disturbed by the azeotropes *B–C* and *B–G*. Although the boiling point of the azeotrope *C–F* is also lower than that of *B*, *C* is entirely removed with the first azeotrope.

2.1 The influence of water on the VLE conditions

The influence of water (*F*) as a potential entrainer on the relative volatilities of azeotropic *B–C* ($\alpha_{B,C}$) and *B–G* ($\alpha_{B,G}$) mixtures was investigated (Tables 2a-2b). Water is already present in the mixture at high concentration, and is readily available.

Table 2: The influence of water on the relative volatility of azeotropic B–C *(a) and* B-G *(b) mixtures*

a.	m_B (kg)	m_C (kg)	m_F (kg)	$\alpha_{B,C}$	b.	m_B (kg)	m_F (kg)	m_G (kg)	$\alpha_{B,G}$
	30	70	-	1		71.5	-	28.5	1
	"	"	25	0.535		"	25	"	0.430
	"	"	50	0.380		"	50	"	0.354
	"	"	100	0.259		"	100	"	0.266

The addition of a moderate amount of water moves both relative volatilities away from 1.0 considerably. The *B–C* volatility order is reversed, and the azeotrope disappears at a moderate water concentration (≈20 mass%). Based on the above results, the BED using water as entrainer was considered suitable for removing *C* and *G* in the fore-cuts more efficiently and with lower *B* loss than the BD.

3. Separation methods

Three separations methods were studied:
1. Traditional batch distillation (reference experiment)
2. BED only during the heating-up of the column, then traditional rectification (BED1)
3. BED during both the heating-up of the column and fore-cuts, then traditional rectification (BED2)

The steps and their stopping criteria are shown in Table 3, where R is the reflux ratio, F_F is the flow rate of water, xd is the condensate composition. The aim of the fore-cut is the removal of *C* and *G*. During the main-cut, high purity *B* is obtained. The goal of taking an after-cut is to reduce *B* loss, as it is recycled to the next batch, and to decrease the organic content of the bottom, respectively. The production process is described in more detail by Hegely et al. (2013).

By the two BED policies, xd_B gradually decreases during the heating-up (Step 1), while xd_C increases. When the *C* concentration hardly changes, Step 2 is started (t_1). Contrary to BD, there is no steady state, but the decrease and stabilisation of the temperatures in the middle section of column indicates the change in the composition. At the end of Step 2, xd_C decreases to its prescribed value, which is indicated by the increase of the top temperature to a value close to the boiling point of *B*, except BED2, where it is slightly higher due to the water content of the distillate. By BED2, water feeding dilutes the mixture from which B is recovered, and can also increase the amount of the fore-cut.

Table 3: The steps and the stopping criteria of the steps for the separation methods studied

Step	Batch distillation	BED 1	BED2
1.	Heating-up of the column	Heating-up with water feeding	
	$R=\infty$	$R=\infty$, $F_F > 0$ after vapour reaches the feed plate	
Stop. crit.	Reaching steady state	xd_B stops decreasing	
2.	Fore-cuts	Fore-cuts without water feeding	Fore-cuts with water feeding
	High R	High R, $F_F = 0$	High R, $F_F > 0$
Stop. crit.		xd_C decreases to a prescribed value	
3.		Main-cut	
		Moderate R	
Stop crit.		xd_F increases (top temperature increases)	
4.		After-cut	
		High R	
Stop crit.	Bottom temperature approaches the boiling point of water		

4. Laboratory experiments

One laboratory experiment was performed at atmospheric pressure for all separation methods, in a glass column (Figure 1) of internal diameter of 5 cm, with a packing height of 1.6 m. The diameter of PROPAK random packing: 0.41 cm. The still (2 dm^3) was heated by a heating basket (nominal heating power: 400 W). The reflux ratio can be set by the aid of a timer and an electromagnet. Temperatures were measured at four different column heights, at the top and in the still. In the BED experiments, one of the thermometers was removed during water feeding, and the stub was used as the water inlet point. The flow rate of the water feeding (25 °C) was determined by preliminary simulations. The analysis of the organic compounds was performed by gas-chromatograph (Varian CP3800, column: CP-Sil-5CB; length: 30 m, diameter: 0.32 mm). The water content was determined by Karl-Fischer method.
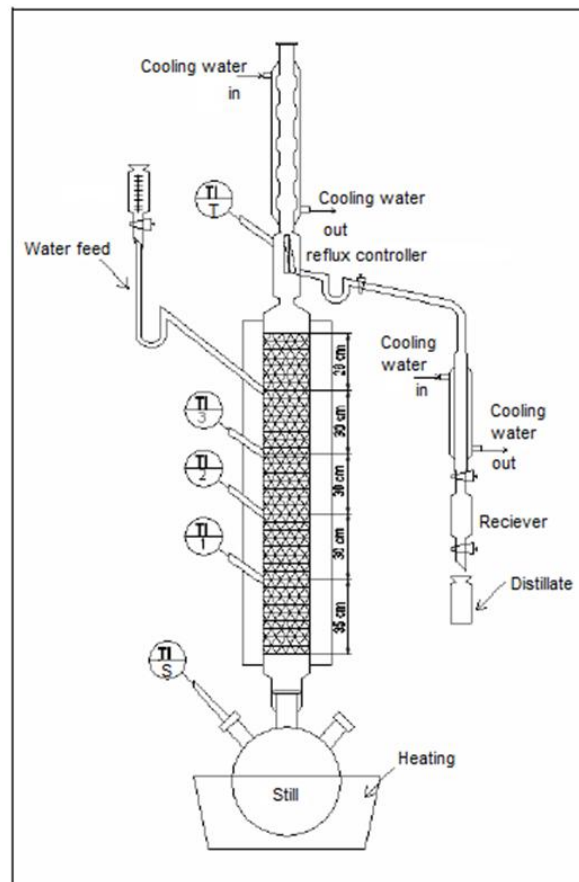

Figure 1: The laboratory batch distillation column with water feeding

4.1 Batch distillation experiment

The first experiment was a traditional batch distillation, without after-cut. The amount of the charge was 886.4 g, its composition: 0.04 mass% *A*, 58.2 % *B*, 1.82 % *C*, 0.14 % *D*, 0.11 % *E*, 38.8 % *F*, 0.88 % *G*. The heating-up lasted 154 min. The reflux ratios were 5.5 during the fore-cut (102 min) and 2.2 during the main-cut (84 min). The cuts were taken in the form of fractions. Based on the results of the chemical analysis, many fractions of the fore-cut were considered to be already part of the main-cut due to their high *B* content. The recovery of *B* was 67.4 % with a purity 99.8 mass%.

4.2 BED1 experiment

The second experiment was made by BED1. The charge had the same composition as in the previous experiment, but its mass was higher (1,332.0 g). Water feeding was started after 31 min of operation and lasted for 61 min with a flow rate of 274 cm^3/h. The reflux ratios were 5.6 during the fore-cut (69 min), 2.2 during the main-cut (158 min), and 5.7 during the after-cut (12 min). The *B* recovery was 95.0 % with a purity 99.8 mass%, by the addition of 279 cm^3 water, which did not increase the liquid volume in the still. Figure 2 shows the evolution of the measured top vapour composition (time zero is the start of water feeding). The xd_B was moderate during heating-up and started to increase rapidly during the main-cut, while xd_C decreased and xd_G had a maximum. The main-cut is finished when xd_E and xd_F in the distillate began to rise.
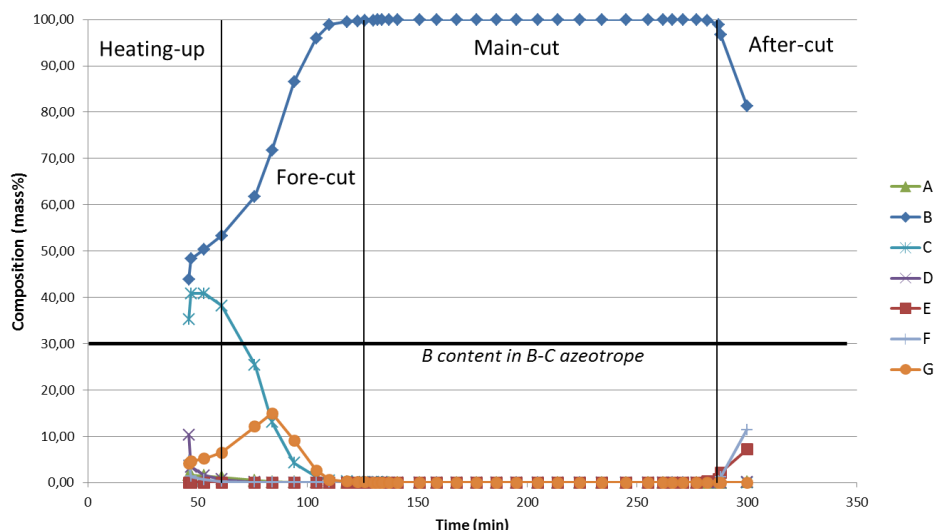

Figure 2: The evolution of measured top vapour composition (BED1 laboratory experiment)

4.3 BED2 experiment

The third experiment (BED2) was performed on a mixture with slightly different composition (0.04 % *A*, 59.2 % *B*, 1.84 % *C*, 0.04 % *D*, 0.07 % *E*, 37.2 % *F*, 0.90 % *G*), whose mass was 1,111.4 g. Water feeding was started after 25 min with a flow rate of 286 cm^3/h. After 50 min of water feeding, the taking of fore-cut fractions was started and the flow rate was reduced to 205 cm^3/h. The reflux ratio was 5.5 during the fore-cut (58 min). Between the fore-cut and the main-cut, a 32 min long period of total reflux operation without water feeding was applied. The average reflux ratio was 2.1 during the main-cut. The same value was applied during the after-cut (11 min), as well. The recovery was 83.4 % with a purity of 99.6 mass%, which is higher than that of the BD experiment, but lower than that of BED1, even though the amount of water fed was higher (436 cm^3). Once again, the water feeding did not increase the still liquid volume.

Both BED experiments highlighted an additional advantage of BED, namely that the heating surface of still was covered by liquid even at the end of operation, unlike BD where it became partially dry.

5. Rigorous simulation of laboratory experiments

The rigorous dynamic simulation of the laboratory experiments was performed using the CHEMCAD professional flow-sheet simulator. The charge data, the reflux ratios, and the duration of the operation steps were given based on the measured values. The heat duty of the different steps was calculated on the basis of the measured average distillate flow rate and the reflux ratio. The theoretical plate number was taken as 14 (including the still), the feed location was the fourth plate (counted from the top). For

column hold-up, the value of 15 cm^3/plate was used. The hold-up and theoretical plate number were determined by previous experiments.

Figure 3 presents the evolution of the calculated top vapour composition for BED1. The results show an acceptable agreement with the measured values. The greatest differences can be observed in the heating-up period. The xd_C shows good agreement, but the calculated xd_B is much lower. This can be explained by higher xd_G and surprisingly high xd_D. However, the low xd_D values measured could be explained by the influence of sampling. The first sample, which has a high (10.3 mass%) D content, contains approximately the half of the total amount of D in the mixture.
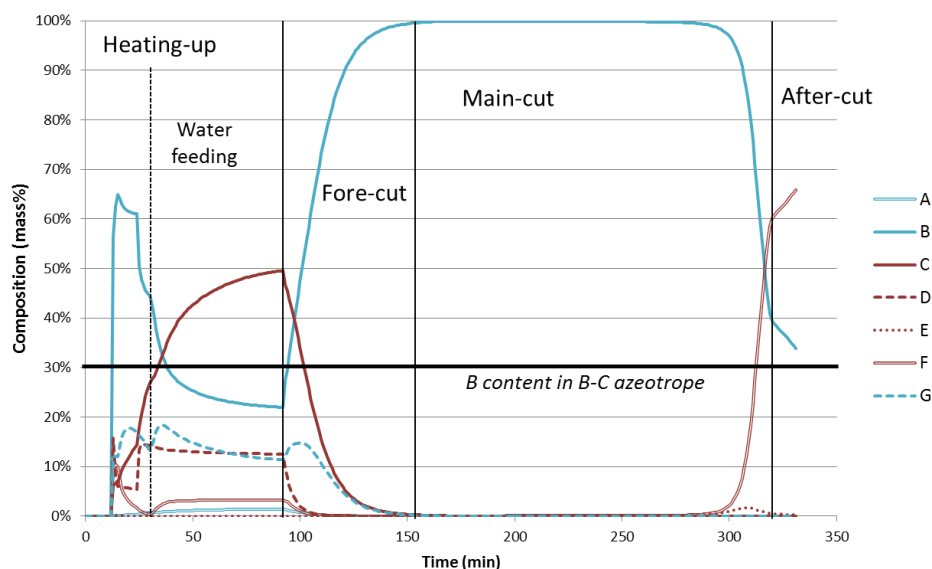

Figure 3: The evolution of calculated top vapour compositions (BED1 laboratory experiment)

The effect of water feeding can be clearly seen on xd_B at the end of the heating-up period (t_1), that is, at the start of production: it is 39.4 % by BD, while only 21.9 % and 27.9 % by BED1 and BED2. To compare the measured and calculated recoveries, the values without correction are used, that is, the original classification of the fractions as fore- or main-cut is respected. The calculated values are close to the measured ones (Table 4), although they are lower in all the cases. The order of the separation methods is the same, that is, the greatest recovery can be obtained by BED1, while BD is the least effective.

Table 4: The calculated and measured recoveries of the laboratory experiments

Method	Measured	Calculated
BD	53.6 %	52.7 %
BED1	84.2 %	75.1 %
BED2	70.9 %	69.3 %

6. Industrial-size pilot productions

Two industrial-size pilot productions were performed, the first by traditional batch distillation, and the second by BED1. The main data of the industrial 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. The reboiler was heated with steam of 5 bar. The holdup of the condenser is 0.5 m^3, that of the column: 1.5 m^3. Based on preliminary calculations and the possibilities available, water (1.1 m^3/h, no preheating) was fed into the reflux stream.

The results for the BD production can be seen in Table 5. B was produced with a high purity and a recovery of 68.5 %. The xd_B at t_1 (22.87 mass%) was already lower than the B content in the B-C azeotrope, and much lower than it was in the laboratory experiment (52.2 %). This can be explained by the accumulation of the low concentration organic pollutants in the condenser, as a result of the high relative hold-up of condenser (2 vol% of charge) and higher theoretical plate number of the industrial column.

By the industrial-scale BED1 experiment (Table 6), water feeding was started after 55 min of operation. B was produced with recovery increased (73.1 %), and in a very high purity. The xd_B was significantly lower

(1.82 %) than by the BD production, due to the water feeding that increased the concentration of *C, G* and water, as well. Consequently, the relative amount of *B* loss in the fore-cut was reduced from 15.6 % to 12.1 %. Because of the high position of water feeding, xd_F was high during the taking of fore-cut, and thus the water content of the fore-cut was also much higher than by BD. BED had lower specific energy demand than BD, as besides the increased recovery, its operation time was even shorter by 10 min.

Table 5: Results of the industrial- scale BD experiment

	Duration (min)	Reflux ratio	Mass (kg)	*A* (mass%)	*B*	*C*	*F*	*G*
Charge	-	-	23,525	0.06	33.32	4.38	61.4	0.83
Heating-up	220	∞	-	-	-	-	-	-
Condensate at t_1	-	-	-	1.78	22.87	71.04	0.06	0.69
Fore-cuts	650	7.33	2,472	0.00	49.56	42.16	0.14	6.85
Main-cuts	740	2	5,379	0.00	99.85	0.00	0.04	0.01
After-cut	105	3	674	0.00	81.74	0.00	17.55	0.07

Table 6: Results of the industrial- scale BED experiment

	Duration (min)	Reflux ratio	Mass (kg)	*A* (mass%)	*B*	*C*	*F*	*G*
Charge	-	-	23,320	0.07	37.14	4.89	56.3	1.56
Heating-up	205	∞	-	-	-	-	-	-
Condensate at t_1	-	-	-	1.44	1.82	78.43	7.4	8.85
Fore-cuts	575	5.25	2,779	0.00	37.88	42.90	3.88	16.37
Main-cuts	840	2	6,328	0.01	99.93	0.00	0.04	0.00
After-cut	85	2	583	0.00	83.68	0.00	15.1	0.02

7. Conclusions

The recovery of methanol from a multicomponent aqueous waste solvent mixture was studied. The components form several minimum azeotropes, which limit the recovery of methanol by traditional batch distillation (BD), by causing a significant loss of methanol.

As the addition of water showed favourable effect on the VLE conditions, the batch extractive distillation (BED) separation of the mixture was studied. A new BED operational policy was suggested, where water (entrainer) feeding was applied only during the heating-up of the column (BED1). At the end of the heating-up, the concentration of organic pollutants increased (compared to BD) and methanol concentration decreased significantly in the top of the column. Water feeding can continue during the fore-cut (BED2), but this increases the amount of fore-cut and dilutes the mixture from which methanol is recovered.

Laboratory experiments were performed in a packed column to compare the BD and the two BED operational policies. The highest recovery was obtained by BED1, the lowest one by BD. The posterior rigorous dynamic simulation of the experiments was made with a professional dynamic flowsheet simulator, which gave the same order of separation methods with respect to recovery. Industrial-size pilot productions of BD and BED1 were performed in a 50 bubble cap tray column. By BED1 the recovery increased from 68.5 % to 73.1%, which is explained by the significant decrease of methanol concentration in the distillate at the end heating-up period by BED, and thus lower methanol loss in the fore-cut. The specific energy demand of the BED production was also lower than that of BD.

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