SEPARATION OF MAXIMUM AZEOTROPES IN A MIDDLE VESSEL COLUMN

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The operation and performance of the middle vessel column were studied by rigorous simulation performed with a professional simulator. The separation of a maximum boiling azeotropic binary mixture (acetone-chloroform) was investigated. This mixture was separated by batch extractive distillation using toluene as solvent. The separation steps were determined and studied. The results obtained were compared with those of the traditional batch rectifier.

KEYWORDS: extractive distillation, middle vessel column, rigorous simulation

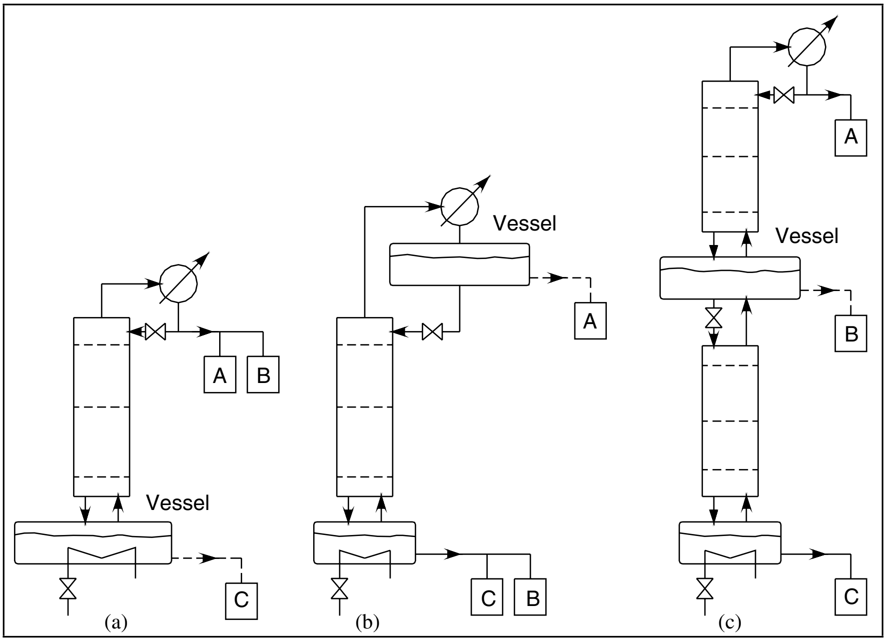
INTRODUCTION

The distillation is a widespread method for the separation of liquid mixtures. The separation is based on the difference of the volatility of the components. Batch distillation is a very frequent separation process in the pharmaceutical, fine-chemical and specialty industries. It is preferable to continuous distillation when the composition and quantity of the mixture to be separated (charge) varies widely from period to period. The simplest and most frequently used bath distillation configuration is the batch rectifier (BR). The nonconventional configurations (e.g. batch stripper and middle vessel column) received great attention at the level of research in the last decade (Kim and Diwekar, 2001) but to our best knowledge they have not been applied yet in the industry.

The operation of the different configuration is presented for the separation of a ternary zeotropic mixture where the order of decreasing volatility is ***A***, ***B***, ***C*** (Figure 1). Each configuration needs heating at the bottom (reboiler) and cooling at the top (condenser) of the equipment.

In the case of a batch rectifier (BR) the charge is filled in a heated, great volume vessel (reboiler) which is located under the column (Figure 1a). The major part of the separation is performed by the column (equipped with a condenser), where the vapour (continuously arriving from the reboiler, having varying composition) is separated to distillate and liquid flowing back to the reboiler. Hence the BR can be considered as a bottom vessel column, as well. In the distillate first ***A*** (1st cut) then ***B*** (2nd cut) can be obtained as product. ***C*** remains in the vessel and can be gained in the residue. Since in the product stream (distillate) the more volatile components are enriched, each stage temperature increases with the time.

In the case of a batch stripper (BS) the vessel ensuring the feed arriving at the top stage of the column is located above the column (Figure 1b), therefore this equipment can be considered as a top vessel column. The charge is filled in this top vessel. The condensate coming from the condenser is also introduced to here. The product is continuously



a. batch rectifier *b. batch stripper* *c. middle vessel column*

Figure 1. Batch distillation column configurations

withdrawn from the partial reboiler at the bottom of the column. Hence first ***C*** (the heaviest component) then ***B*** can be obtained as product. The lightest component ***A*** remains in the vessel. Since in the product stream (bottoms) the less volatile components are enriched each stage temperature decreases with the time contrary to the BR. The most important operational parameter is the reboil ratio (instead of the reflux ratio).

The middle vessel column (MVC) is a combination of the BR and BS (Figure 1c). The charge is filled in the vessel located at the middle of the column between two column sections. From the middle vessel (MV) the liquid of varying composition is fed to the top stage of the lower (stripping) section. Both the liquid leaving the bottom stage of the upper (rectifying) section (RS) and the vapour leaving the top of the stripping section (SS) are introduced into the middle vessel (MV). The vapour leaving the vessel arrives at the bottom of the rectifying section. The vessel can be considered as a stage with great, varying hold-up. Products are continuously withdrawn from both the top (***A*** can be produced in the distillate) and the bottom (***C*** can be produced in the bottoms). At the end of the operation in the middle vessel ***B*** can be enriched. The most important operational parameters are the reflux (R) and reboil ratios (R_s).

Due to the increased number of operational parameters the MVC can be operated in a more flexible way than the BR and BS. The number of degrees of freedom and the operational flexibility of the MVC can be further increased by

- heating or cooling of the vessel (Figure 2),
- introducing one part of the liquid (b_L) leaving the rectifying section directly to the stripping section bypassing the vessel,
- introducing one part of the vapour (b_V) leaving the stripping section directly to the rectifying section bypassing the vessel.

Depending on the value of the by-pass ratios b_L and b_V different versions of the MVC can be distinguished: a. basic: $b_L = 0$ $b_V = 0$; b. liquid by-pass: $b_L = 1$ $b_V = 0$; c. vapour by-pass: $b_L = 0$ $b_V = 1$.

For the separation of two components (***A*** and ***B***) forming an azeotrope a special distillation method must be applied such as the extractive distillation (ED). In this case a third component, a separating (extractive) agent (solvent, ***E***) is added to the mixture which makes the separation of ***A*** and ***B*** possible without the formation of new azeotropes. The solvent has usually much higher boiling point than the original components.

The performance and feasibility of the ED separation of minimum azeotropes in the (conventional) batch rectifier (BR) were investigated by Lang et al. (1994) and Lelkes et al. (1998). The separation of maximum azeotropes by ED in a BR was investigated by Lang et al. (2000a, b). They concluded that more efficient ***A***/***B*** separation can be

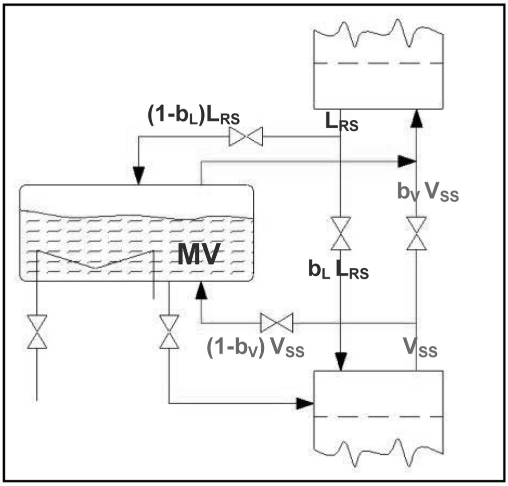


Figure 2. Middle section of a general MVC ($b_L \geq 0$, $b_V \geq 0$)

produced by continuous ***E***-feeding (whose flow rate is denoted by F) when the column contains also an extractive section (ES, plates from the feed plate to the reboiler).

During the last few years much attention was paid to the investigation of non-conventional batch column configurations (stripper, middle-vessel column (MVC), multi-vessel column). The application of the MVC for the ED of minimum azeotropes was proposed among others by Safrit et al. (1995), Warter et al. (1999, 2004), Hilmen (2000), Low and Sorensen (2002) and Cui et al. (2002). Warter and Stichlmair, Low and Sorensen obtained the best results with the liquid by-pass version (Figure 3).

The aim of this paper is to study the operation and performance of the (liquid by-pass version of) MVC by rigorous simulation for the ED of a maximum boiling azeotropic mixture (acetone (***A***) – chloroform (***B***) + toluene (***E***)) and to compare the results of MVC with those of the BR.

The residue curve map and the batch regions of the ternary mixture are shown in Figure 4.

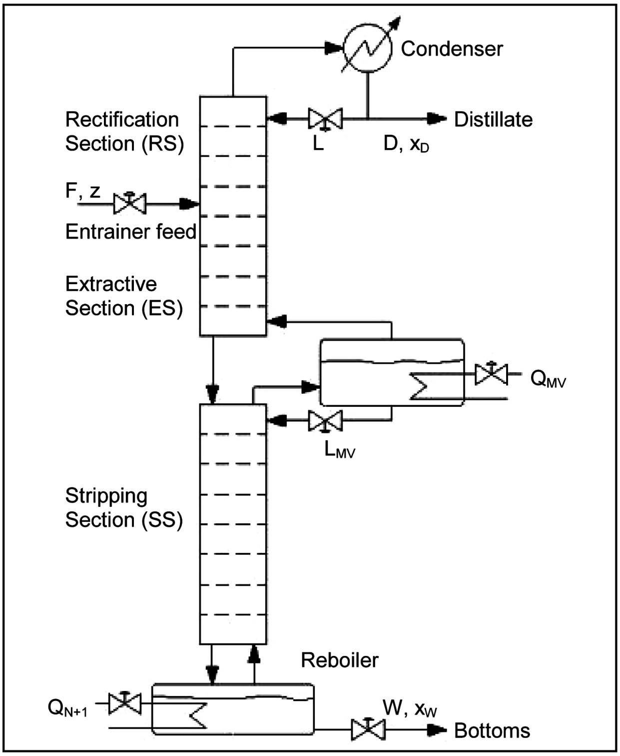


Figure 3. Extractive MVC (liquid bypass version)

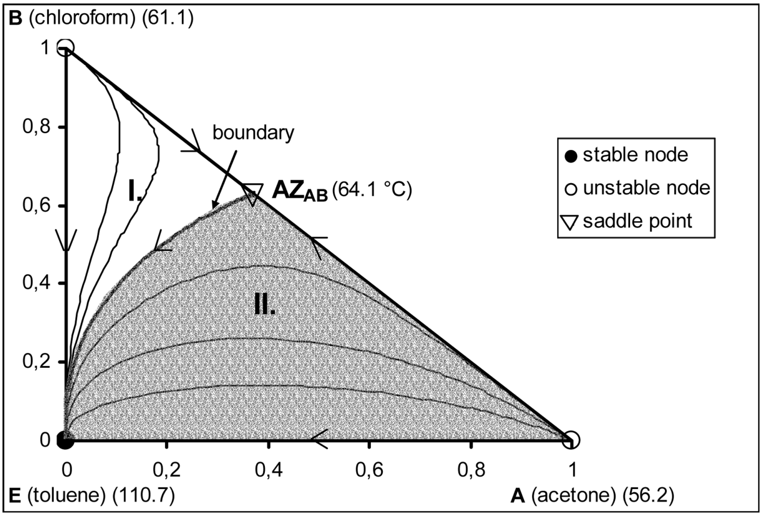


Figure 4. The residue curve map and batch distillation regions

SEPARATION STEPS

For both configurations we determined all separation steps (including the optional off-cuts) taking into consideration the main separation steps (without off-cuts) suggested for the BR by Lang et al. (2000a). The separation steps are as follows

0. Addition of a small quantity of ***E*** (SF0) to the azeotropic charge.

By mixing the charge with the entrainer the vessel composition is brought into the BD region II (Figure 4, darkened area).

1. Start-up without product withdrawal and without ***E***-feeding ($R = \infty$, $F = 0$ and for the MVC $R_S = \infty$).

At the end of this step pure ***A*** can be reached in the distillate since the vessel composition is located in the BD region II. Hence there is no need for a purification step before the ***A***-production (contrary to the separation of minimum azeotropes in this case the α-limit is vertex ***A*** and not the azeotrope). At the end of this step the column may operate under steady state conditions. (The start-up can be carried out also under $F > 0$ (Hilmen, 2000). In this case Step 0 can be omitted and at the end of Step 1 there can not be steady state.)

2. Production of ***A*** (in the distillate) under continuous ***E***-feeding and (for the MVC) bottoms withdrawal ($L_{MV} \approx D$, $W = F$).

Due to the continuous feeding the vessel-path can cross the BD region boundary therefore higher recovery of ***A*** can be reached (for a given product purity) than by the traditional BD (batch addition of the whole amount of ***E***). Theoretically it is possible to produce simultaneously ***A*** (in the distillate) and ***E*** (in the bottoms) and to accumulate ***B*** in the MV (simultaneous separation scheme) but on the basis of our experiences being in agreement with those of Hilmen (2000) the sequential scheme can much more easily performed than the simultaneous one. At the end of this step the ***E***-feeding is stopped.

3. Purification of the distillate (from ***A***) under infinite reflux ratio ($R = \infty$, $F = 0$) and for the MVC $L_{MV} = 0$, $W = 0$.

   At the end of Step 2 $x_{D,A}$ is still high. If we want to produce ***B*** in high purity a short purification period can be necessary.

4. Production of ***B*** (in the distillate) under $R < \infty$ and $F = 0$.

   In this step we perform separation $\boldsymbol{B}/\mathrm{AZ}_{AB}$ in the RS (BR: all plates in the column MVC: all plates above the MV).

   This step is stopped when $x_{D,B}$ falls to its prescribed value (or the middle vessel is empty). The regeneration of the entrainer can be simultaneously performed with the production of ***B*** ($L_{MV} \approx D + W$).

5. The removal of ***A*** and ***B*** as an off-cut (distillate) under reduced R and $F = 0$.

   This step is stopped when $x_{D,E}$ reaches its purity prescribed.

   In the case of the MVC the bottoms collected during Step 2 is filled in the middle vessel at the beginning of this step.

RIGOROUS SIMULATION CALCULATIONS

We studied the operation and performance of the (liquid by-pass version of) MVC by rigorous simulation for the ED of a maximum boiling azeotropic mixture (acetone (***A***) − methanol (***B***) + toluene (***E***)) and we compared the results of MVC with those of the BR.

MODEL AND METHOD OF SOLUTION

The model applied is based on the following simplifying assumptions:

- theoretical stages,
- negligible vapour hold-up,
- constant volume of liquid plate hold-up (excepted the vessel and the partial reboiler of the MVC).

The model equations to be solved are well known:

a. Non-linear differential equations (material balances, heat balances)
b. Algebraic equations (vapour-liquid (VLE) equilibrium relationships, summation equations, hold-up equivalence, physical property models).

For the solution of the above equations we used the DYNCOLUMN (column sections, simultaneous correction method) and DYNAMIC VESSEL (vessel and product tanks) modules of the CHEMCAD 5.5.0 professional simulator (Figure 5) (Chemstations, 2005).

EXAMPLE

The column contains 30 theoretical stages (+ total condenser + reboiler + (for the MVC) middle vessel). The entrainer feed stage is the 5th for the BR and the MVC. The liquid

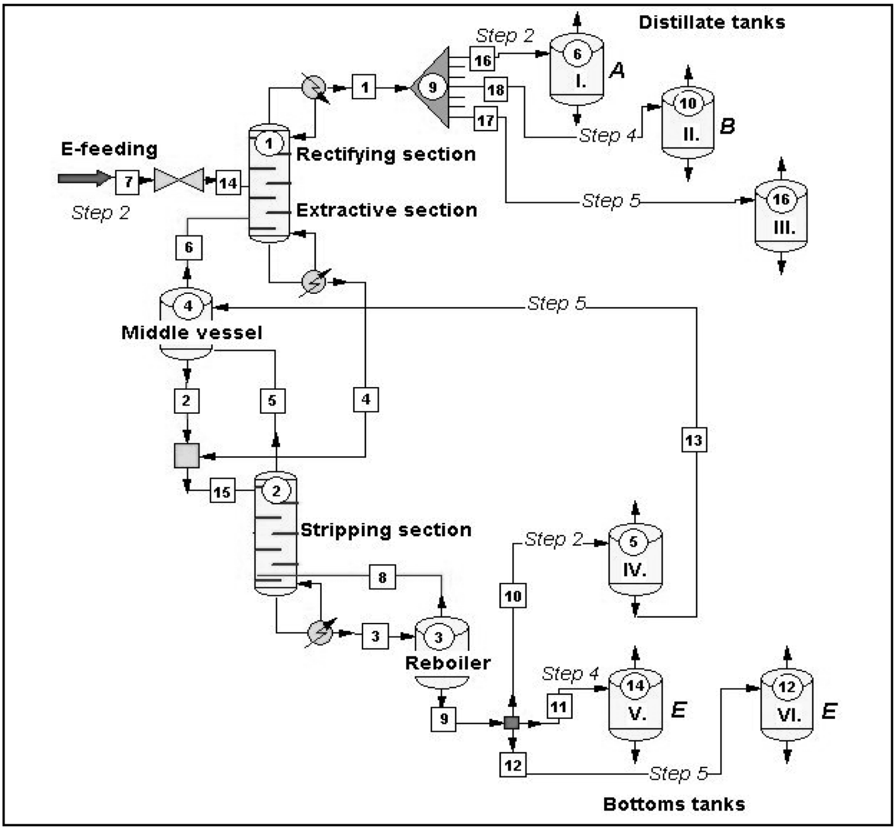


Figure 5. The ChemCad simulation flowsheet

from the MV is introduced to plate 21. Operational parameters: $Q_{N+1} = 1.5$ kW, hold-up: 46 cm^3/plate (except for the reboiler). The value of the reflux ratio: 20 (Step 2), ∞ (Step 3), 20 (Step 4), 5 (Step5).

For the MVC the values of the liquid flow rate from the MV (L_{MV} in mol/h): 0 (Step 1), 10.1 (Step 2), 0 (Step 3), 15.6 (Step 4), 47.74 (Step 5) and those of the bottoms flow rate (W in mol/h): 0 (Step 1), 45.28 (Step 2), 0 (Step 3), 8 (Step 4), 21.08 (Step 5).

The quantity of the binary charge (U_{ch}) is 78 moles (6 dm^3). The charge has the azeotropic composition ($\boldsymbol{x}_{ch} = [0.367, 0.633, 0]$).

The entrainer is pure, boiling point liquid. In Step 0 22.6 moles of $\boldsymbol{E}$ (2.42 dm^3) is added to the charge. The flow rate of $\boldsymbol{E}$-feeding in Step 2: $F = 45.28$ mol/h (4.79 dm^3/h).

Table 1. The composition of the products for the MVC and for the BR (*Italic*)

				Content of distillate tanks, mol								
	Vessel, mol			I.			II.			III.		
Step	A	B	E	A	B	E	A	B	E	A	B	E
0	28.63	49.37	22.6									
	28.63	*49.37*	*22.6*									
1	24.84	48.91	11.98									
	17.90	*42.51*	*22.54*									
2	8.16	36.52	14.01	20.83	0.48	0.01						
	1.90	*39.81*	*146.33*	*23.96*	*0.65*	*0.01*						
3	9.32	35.68	13.79									
	1.70	*35.16*	*149.89*									
4	5.36	10.16	0.54				0.58	24.44	0.00			
	0.00	*1.32*	*147.21*				*0.95*	*38.28*	*0.00*			
5	0.00	0.00	25.11							11.27	30.76	16.29
	0.00	*0.05*	*115.81*							*3.71*	*10.39*	*22.40*
				Content of bottoms tanks (MVC), mol								
				IV.			V.			VI.		
2				0.20	8.57	102.12						
4							0.00	0.02	23.04			
5										0.00	0.15	44.13

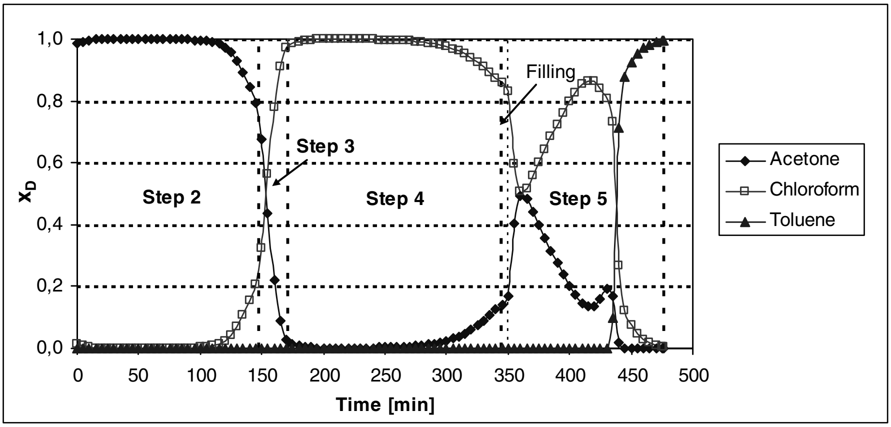
The purities prescribed: ***A***: 0.975 ***B***: 0.975 ***E***: 0.995. The stopping criteria for Step 3: $x_{D,B} > 0.975$.

The duration of filling of the MV (at the beginning of Step 5) is 6 min. (In this period $R = \infty$, $L_{MV} = 0$, $W = 0$.) The results obtained by MVC and BR under the same toluene consumption are shown in Table 1.

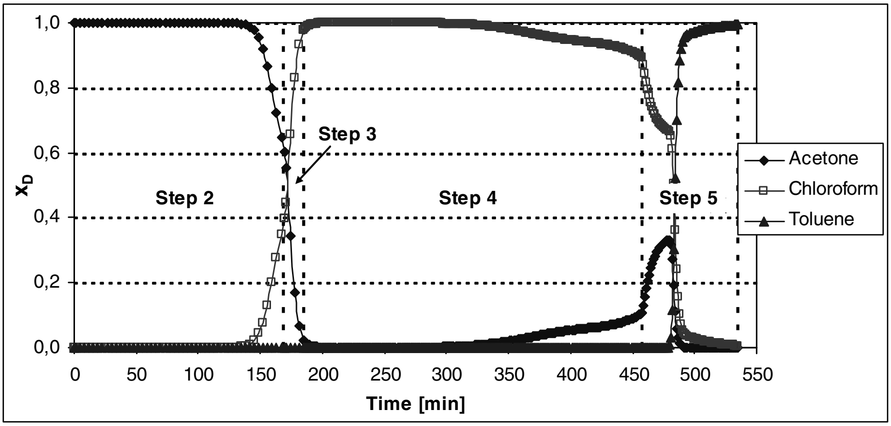
Due to the amount of ***E*** added in Step 0 at the start of Step 2 $x_{D,A}$ was high in both cases (in the case of MVC it contained 1.5% ***B***) (Figure 6).

The most difficult separation (***A***/***B***) was successfully performed by both configurations. By the MVC we were able to produce ***A*** of prescribed purity with lower recovery (72.7%) than by the BR (83.7%). For the separation ***A***/***B*** less stages are available in the MVC ($N_{ES} = 15$ instead of 25). The entrainer withdrawn as bottoms in Step 2 contained 7.7% ***B***. It had to be purified later (in Step 5, sequential scheme). In the stripping section due to the high flow rate of ***E***, which is withdrawn as bottoms, the reboil ratio (3.3) and also the number of stages ($N_{SS} = 10$) were moderate.

In Step 3 in both cases $x_{D,B}$ increased quickly. In Step 4 the production of ***B*** was also successfully performed by both configurations. By the MVC we were able to produce ***B*** of prescribed purity with lower recovery (49.5%) than by the BR (77.5%). For the $\boldsymbol{B/AZ_{AB}}$



(a) MVC



(b) BR

Figure 6. The evolution of the distillate composition

separation less rectifying stages are available in the MVC ($N_{RS} = 20$ instead of 30). However in the MVC the entrainer (not withdrawn in Step 2) was successfully regenerated in this step, as well.

In Step 5 the regeneration of ***E*** was successful in both cases. The loss of ***E*** (for the whole process) was somewhat lower for the MVC (14.7%) than for the BR (17.6%). The detailed results of the calculation are shown in Table 1 (the results for BR are written with Italic characters).

It must be emphasized that in the given example the (open loop) operation of the BR and the MVC was not optimised. Their performance (e.g. the recovery of *B*) could be considerably improved by optimisation and/or (closed loop) control (mainly in the case of MVC, where the degree of freedom is higher) that we intend to study in the near future.

CONCLUSION

The operation of the liquid by pass version of the middle vessel column (MVC) was simulated for the batch extractive distillation (BED) separation of a maximum boiling azeotropic mixture. The MVC column proved to be suitable also for the BED separation of maximum azeotropes. The MVC is a very flexible configuration because of its great degree of freedom. However by our experiences it is much more difficult to operate this very sophisticated configuration in a proper way than the traditional BR. Besides the number of stages of the stripping section of the MVC can be ensured to the detriment of that of the other section(s).

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