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DEVELOPMENT OF A HYBRID SOLVENT RECOVERY PROCESS (COMBINATION OF DISTILLATION AND VAPOUR PERMEATION)

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INTRODUCTION

For the development of a new process for a specialty chemicals producer an adequate solvent recovery plant for the accumulated mixture of alcohols and water has to be designed. The customer asks in an early stage of its own laboratory and pilot plant process development for the conceptual design of the solvent recovery plant. The following lecture shows the main steps of this development from the first compilation of properties for short cut calculations based on literature and data bases up to results from the start up assistance and operation experience of the built solvent recovery plant. Beside the discussed separation concepts also other designs were discussed during the development with the customer, but will not be shown due to time limitation. Different process alternatives will be compared based on the operation mode, recycling grade and process costs. Due to a secrecy agreement it is unfortunately not possible to talk about details of the customer process and about the different chemicals and solvents which are used in it. Therefore synonyms are used for the components. Nevertheless even with these synonyms the typical steps of such a development can be discussed.

PROCESS FUNDAMENTALS

The accumulated mixture of alcohols and water (and some high boiling side products of the process) consists mainly of three different alcohols and water. One of these alcohols is used as the solvent for the synthesis. This one is the high boiling alcohol (in the following the synonym HBA is used for it). This alcohol has a purchase price of around 5–6 Euro/kg. Therefore a high recycle rate of this component was fundamental for the recovery. A second important criterion is the water content of the recovered alcohol which should be less than 500 ppm. With considerable higher water content the yield of one of the synthesis reaction steps will decrease noticeable. For a typical batch approx. 5 t of the HBA are needed.

Table 1. Boiling sequence in the system

Component	Comment
LBA	
MBA/Water	Homogeneous Low boiler azeotrope
MBA	
HBA/Water	Heterogeneous Low boiler azeotrope
HBA/Water/LBA	Heterogeneous Low boiler azeotrope
Water	
HBA	
P-Chlornitrobenzol*	
Bernsteinsðurediisopropylester*	
P 16188*/**	

*keine Binðrdatensðtze angelegt
**Daten von C32H66 kopiert !!

The medium boiler alcohol (MBA) is produced in one of the reaction steps of the process (approx. 350 kg per Batch). Because of the small produced volume of this alcohol it should be recovered with small amount of impurities to sell that as a side product or to minimize the disposal costs.

The third alcohol (low boiling alcohol LBA) and water are used as washing agent for the produced solid chemical. This component has a lower purchase price than the HBA but the amount of one typical batch is approx. 17 t. Therefore also here a high recovery rate was necessary.

The Table 1 shows the boiling sequence of the mixture with LBA as the lowest boiler in the system. This table was the result of one of the first tasks during the process synthesis for the new plant. The VLE data was taken from literature, Dortmunder Data Bank and in-house data. For the binary system HBA/MBA the VLE was estimated using Unifac. For the first conceptual calculations and process simulations the data were sufficient.

The MBA and water form a homogeneous azeotrope. HBA and water and the ternary mixture of HBA, LBA and water form heterogeneous azeotropes. HBA is the highest boiling component in the system.

For the solvent recovery plant a continuous flow of 1800 kg/h of this mixture was the basis for the design. The mixture consists of 70 wt. % LBA, 17 wt. % water, 11 wt. % HBA and approx. 0.7 wt.% of MBA. Besides the discussed specification for the different solvents the plant should also have an outlet for high boiling components as e.g. NaOH.

SEPARATION CONCEPTS

In the following different process alternatives for the recycling plant which were developed during conceptual design will be discussed and compared based on operation mode, recycling grade and process costs.

CONVENTIONAL DISTILLATION

The first developed separation scheme is shown in Figure 1. This is a conventional distillation train with a low boiler column combined with a classical heterogeneous azeotropic distillation. The feed enters the low boiler column where the LBA will be distilled as top product. The MBA will be separated as a side draw from the LB-column. The bottom product of this column consisting of water and the HBA is a two phase mixture and will be fed into a liquid liquid separator.

From here the two phases are fed into two stripper columns. Water will be separated as the bottom product of the water stripper. The HBA will be gained as a side product above the bottom of the HBA column. With this configuration high boiling components which are water soluble (e.g. NaOH) will leave the train together with the water. Organic (water insoluble) components leave the train as bottom product of the HBA stripper and will not affect the quality of the recovered HBA.

The top product of the two columns is the heterogeneous azeotrope which is formed between water and HBA. After condensation this will be fed again to the liquid liquid separator. Simulation of the LB column indicated that this column should be operated under vacuum. The Table 2 shows the simulation results of a pressure variation with the specified separation of the LBA.

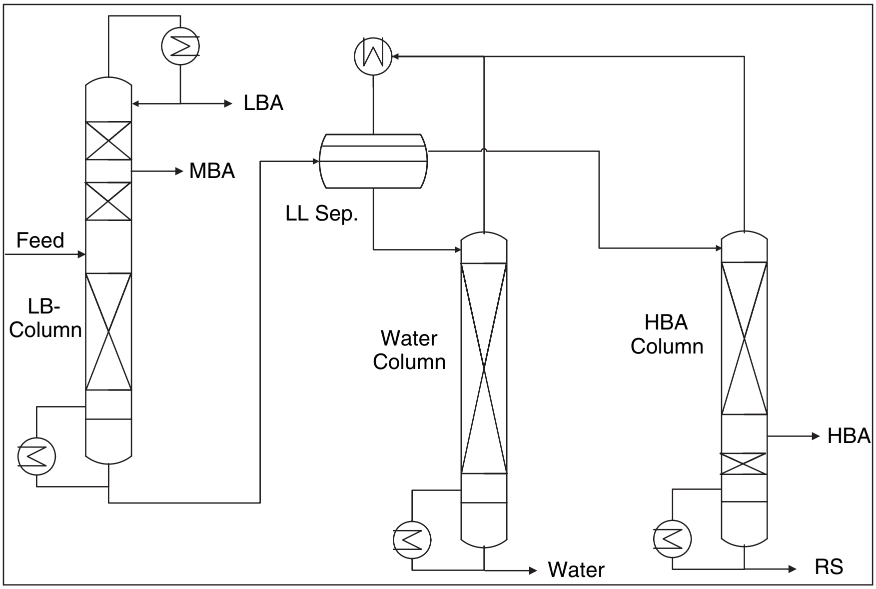

Figure 1. Conventional distillation scheme

Table 2. Pressure variation

Pressure [mbara]	Stages
400	33
600	46
700	62

The main advantages of this separation scheme are:

- The high recovery rate for HBA (>96 %),
- The low energy consumption,
- No necessity for an auxiliary component (e.g. entrainer)
- Easy heterogeneous distillation (five theoretical stages for the water stripper, and eight theoretical stages needed for the HBA stripper)

The main disadvantages of this separation scheme are:

- The high effort for the separation of the LBA (vacuum 400 mbara needed)
- HBA is a bottom product
- High experimental effort needed to validate the scheme (open questions LB column, influence of unknown impurities on the distillation and liquid liquid separation)

Considering these results the customer decided to focus on other possible separation concepts (azeotropic and extractive distillation). In the following the results for an extractive distillation scheme will be discussed.

EXTRACTIVE DISTILLATION

The first step considering extractive distillation is the entrainer selection. The entrainer for this process should influence the relative volatility between water and the HBA in a way, that there is no longer an azeotrope formed between these two components. Beside the influence on the separation of the entrainer other aspects as selectivity (how much entrainer is needed), economical (price for the entrainer), properties (e.g. boiling and melting points of the entrainer which can qualify or disqualify the use of these components in the plant), corrosion (special material needed) and safety at work (e.g. toxic or carcinogen behaviour) need to be considered. A good overview for these selection criteria can be found in [1]. For the entrainer selection the DDB Entrainer selection tool was used [2], [3].

The Table 3 shows an extracted result of this search. The different possible entrainers will be compared with the separation factor (separation factor for an azeotrope is 1, the smaller the number the easier the separation) and the selectivity (which is the proportion of the activity coefficient at infinite dilution from water in the entrainer and HBA in the entrainer). The higher the selectivity figure the smaller is the needed total

Table 3. Entrainer selection

Extractive agent	Sep. factor Water/HBA	Selectivity	Comments
Dimethylsulfoxide	0.147	7.33	$T_B = 190$ °C
Ethylenglykole	0.154	6.99	$T_B = 197$ °C
Glycerin	0.229	4.73	$T_B = 290$ °C
Sulfolan	0.289	3.72	$T_B = 286$ °C
Ethanolamine	0.297	3.64	$T_{Melt} = 95$ °C
Aminopyridin	0.307	3.53	$T_{Melt} = 60$ °C
N-Methylformamid	0.345	3.14	$T_B = 185$ °C
M-Phenylendiamine	0.396	2.73	toxic
Brenztraubensäure	0.418	2.59	strong acid
Acetamid	0.441	2.47	carcinogen
Ethylene Cyanohydrin	0.48	2.25	toxic
N-Methylacetamid	0.489	2.21	$T_B = 208$ °C
Propandiamin	0.494	2.20	$T_B = 119$ °C

amount of the entrainer. In the comment line the other points as discussed before are documented.

Based on this search and in-house expertise four possible entrainers can be selected. Due to the fact that our company has build different plants with Ethylenglykole (EG) as entrainer or extractive agent with good experience EG was selected for the following process simulations. EG increases the relative volatility of water, so that it becomes the highest boiler in the alcohol/water system. Therefore the three alcohols will leave the extractive distillation column as top product.

The Figure 2 shows the separation scheme for the extractive distillation using EG as entrainer. The feed enters the extractive distillation (ED) column. EG is fed above the alcohol and water mixture feed stage, therefore the column consists of three different separation sections.

Above the EG feed stage the separation between EG and the alcohols takes place. Between the two feed stages the extractive distillation takes place. Below the alcohol and water mixture feed stage the separation between EG/water and the alcohols is carried out.

The bottom product of the ED column consisting of water and EG will be separated in the EG column where water is the top product. EG will be separated at the bottom of the column and recycled to the extractive distillation column.

Because of the high boiling point of EG a heat integration between the feed of the EG column and the bottom product is reasonable. The top product of the extractive distillation column consisting of the three alcohols is separated in a HBA column were LBA is the top product, MBA will be separated as a side product and HBA is the bottom product of this column.

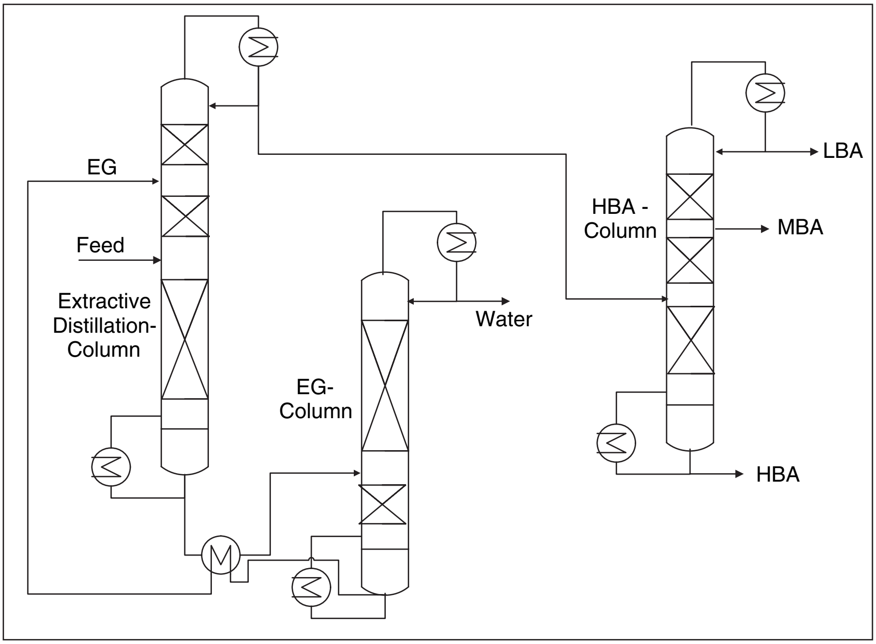

Figure 2. Extractive distillation separation scheme

The HBA recovery rate of this scheme is approx. 93%. The main advantages of this scheme are:

- Easier separation than the conventional scheme (no vacuum needed)
- Less theoretical stages needed as for the conventional distillation (extractive distillation 24, EG column 10 and HBA column 14 theoretical stages)
- HBA is once distilled as top product (high boiler impurities are therefore separated)
- Well known process, only a small amount of experimental validation work was necessary

The main disadvantages of this concept:

- Entrainer recovery necessary (elimination of high boilers which accumulate in the entrainer)
- High energy demand in comparison to the conventional scheme (factor 2, water is separated as a top product)
- Separation of MBA as a side draw leads to an increased loss of HBA, therefore the recovery rate of this process is smaller than that for the conventional one.

SEPARATION STEPS IN THE MAIN PROCESS

At this point of the process synthesis intensive discussions started with the developer of the main process (core business of the customer). Therefore some ideas were discussed to change the concept from an "end of pipe solution" to separation steps in the process itself. The main ideas were:

1. Separation of the MBA during the synthesis. At this point there is no water (and no LBA) in the system and therefore the separation between MBA and HBA is relatively simple. To investigate and to design this separation step in the process it was necessary to investigate the VLE between MBA and HBA experimentally. Test distillations in the pilot plant of the customer showed that this step is feasible.
2. Make use of the heterogeneous azeotrop between water and HBA in the process. As discussed the LBA alcohol is the washing agent in the process and one of the lessons learned from the simulation of the conventional scheme was, that the separation in the ternary system water, LBA and HBA is the toughest separation in the process. Therefore a separation of the HBA out of the process before washing the product with LBA will simplify the separation. Therefore experiments were carried out at the pilot plant of the customer to separate HBA out of the process with a simple steam distillation. The results of these experiments showed no influence on the quality of the produced chemical.

HYBRID PROCESS

Because of the new steam distillation in the process itself the mixture to be separated in the solvent recovery plant was now reduced to a three component system (HBA, MBA and water). After simulation work with different separation schemes it was clear that the most convenient distillation scheme is a three column system analogous to the conventional scheme as discussed before (whereby MBA is the top product of the first column). An alternative to this scheme was the use of a membrane to dehydrate the alcohol mixture. First proof of principle tests with a vapour permeation test kit showed that the dehydration to approx. 1 wt. % water is feasible with a low energy consumption in comparison to the distillation step.

After these results it was decided to install a membrane pilot plant into the customers facilities to run this membrane process (vapour permeation) for some months to investigate the robustness of the process and to give future plant personal the opportunity to experience the specific work with a membrane plant. The result of these pilot plant test run was positive, therefore it was decided to combine for the new solvent recovery plant vapour permeation together with distillation.

The ternary diagram in Figure 3 explains the separation scheme in the built solvent recovery plant. Shown is the ternary system of water, HBA and MBA. The miscible gap between water and HBA, the heterogeneous azeotrop formed between water and HBA and the homogeneous azeotrope between water and MBA are represented in the diagram.

Point 1 represents the composition of the organic mixture after liquid liquid separation. The small difference between the composition of the heterogeneous azeotrop

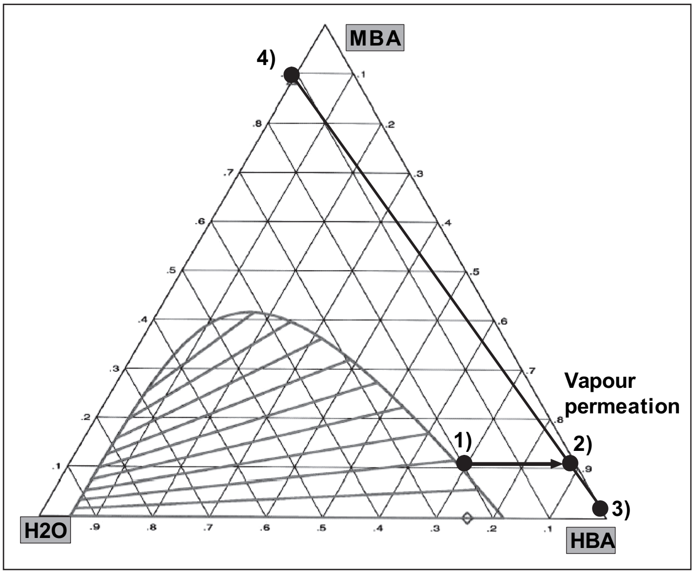

Figure 3. Ternary diagram H_2O, HBA, MBA

and the composition of the organic phase shows the high energy demand for a separation using distillation. The dehydration of the organic phase to an amount of approx. 1 wt. % will be done with the vapour permeation (therefore the mixture has to be evaporated only once).

The separation between HBA (point 3) and the MBA/water azeotrope (point 4) will be done in a distillation column. The homogeneous azeotrope between water and MBA simplified this separation and therefore the discussed separation of MBA from HBA in the process itself was no longer necessary. Instead the amount of MBA was stocked up before entering the reboiler of the vapour permeation to fulfil the mass balance for this separation.

The Figure 4 shows the solvent recovery plant as built. Here the steam distillation step in the process itself is also included. After condensation of the steam distillation the two phase product is fed to a liquid liquid separator. The organic phase is fed (as discussed above) into the reboiler of a vapour permeation plant. At the reboiler of the vapour permeation high boiling residues can be purged out of the process.

The retentate will be fed to the HBA column were the separation between HBA and the azeotrope of MBA/water is taking place. The water phase from the liquid liquid separator will be fed to a simple water stripper known from the conventional concept as discussed before.

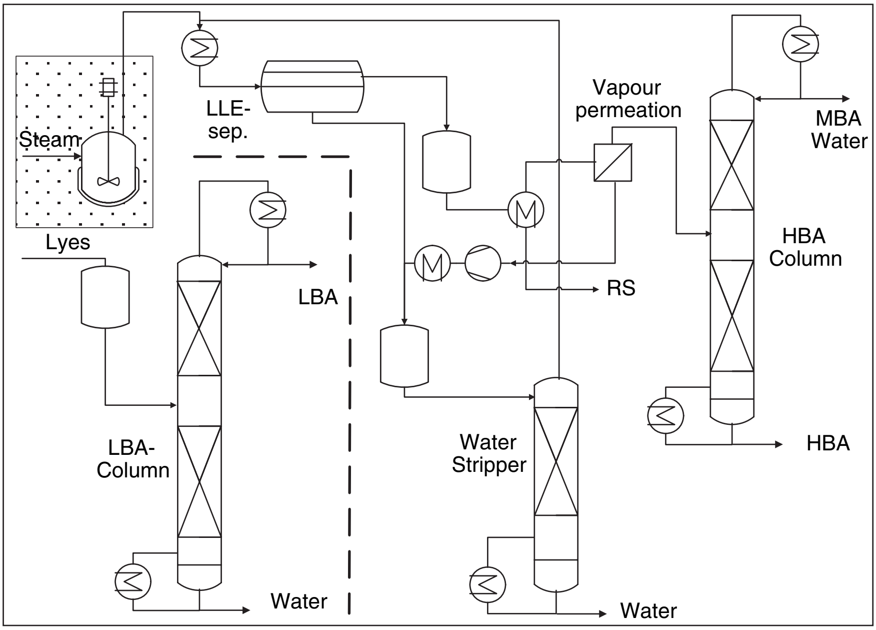

Figure 4. Built solvent recovery plant (hybrid process)

Another result from operation of the membrane unit in the pilot plant was, that the concentration of MBA in the permeate was around 7 wt.%. Due to the high purchase price of this component and the easy water stripper separation it was therefore feasible to fed the permeate to the water stripper.

Also shown in Figure 4 is the remaining easy separation between the LBA and water in a separate distillation column.

The HBA recovery rate of this plant is approx. 99%. The main advantages of this separation scheme are:

- Easy distillation (HBA column 18, water stripper 5 and LBA column 10 theoretical stages)
- Highest recovery rate of all investigated concepts
- Lowest energy consumption of all investigated concepts

The main disadvantage of this hybrid process is the additional process costs due to the fact that the membranes need to be replaced after some years. The process was calculated with a replacement of the membranes every two years. Due to low energy costs of that concept the hybrid process was still the cheapest option.

START UP AND OPERATION EXPERIENCE OF THE HYBRID RECOVERY PLANT

The start up of the new recovery plant was in summer 2004. The main experiences with this plant since that are:

- The pH of the organic phase before entering the reboiler of the vapour permeation needs to be controlled (otherwise problems with material warranty). This set up will be done with an organic acid. At one of the first trials this organic acid was overdosed and fed into the HBA column which leads to separation problems. Here a monitored pH adjustment solved the problem.
- Start up and especially shut down procedure for the membrane plant are more complicated than that for a simple distillation column. For the start up it is important to((??)) build up a pressure (with nitrogen). Otherwise the displacement of the membrane material is possible. High water contents during start up are also problematic due to the mechanical stress of swelling of the polymer material depending on the water content. Therefore the start up of membrane plant is done with a high recycle stream of the retentate.
- After some trials with the HBA column the necessary stock up of MBA for the azeotropic distillation was fixed for the process.
- Up to today (January 2006, approx. 18 operating months) there is no performance loss of the membrane plant detectable.

NOMENCLATURE

LBA	Low boiling alcohol
HBA	High boiling alcohol
LB	Low boiler
MBA	Medium boiling alcohol
EG	Ethyleneglykole
ED	Extractive Distillation

LITERATURE CITED

1. Lee, F. M. and Gentry, J. C.; Don't overlook extractive distillation; October 1997, Chem. Eng. Progr. pages 56–64
2. Gmehling, J. and Möllmann, C.; Synthesis on distillation processes using thermodynamic models and the Dortmunder Data Bank; Ind. Eng. Chem. Res. 1998, 37, 3112–3123
3. Gmehling, J. and Möllmann, C.; Auswahl selektiver Zusatzstoffe für die Rektifikation durch kombinierten Zugriff auf experimentelle und vorausberechnete Gleichgewichtsdaten