

ELUXYL™ Twin Raffinate Technology

Luc WOLFF and Philibert LEFLAIVE

Institut Français du Pétrole
IFP-Lyon
BP 3
69390 Vernaison
FRANCE

e-mail : luc.wolff@ifp.fr or philibert.leflaive@ifp.fr

Keywords : Simulated Moving Bed, Eluxyl™, Twin Raffinate, xylenes

Prepared for presentation at the 2004 Annual Meeting, Austin, November 7-12
Session : Industrial Liquid Phase Adsorption

Copyright ©2004 IFP

Unpublished

AIChE shall not be responsible for statements or opinions contained in papers or
printed in its publications

Introduction

Simulated moving bed (SMB) has been extensively used for forty years as the preferred technology for liquid adsorptive industrial separation. Among the different applications of this technology, the paraxylene recovery from C₈-aromatic cut is the far most known. AXENS_{IFP group technology} ELUXYL™ process is one recent and efficient technology for paraxylene production which has been developed by IFP (Institut Français du Pétrole) and commercialized by AXENS (Ash et al., 1994), (Hotier et al., 2000), (Hotier and Méthivier, 2002).

In its conventional operation, the SMB process is characterized by two inlets, desorbent and feed injections, and two outlets, extract and raffinate withdrawals. These four streams delimit four zones which can be defined as follows : zone 1 is located between desorbent and extract streams, zone 2 between extract and feed streams, zone 3 between feed and raffinate streams and finally zone 4 between raffinate and desorbent streams. Taking into account the target of coproducing several products with the same unit, SMB process may be operated with an additional outlet (second raffinate or second extract) leading to one additional zone.

The objective of this work is to present the results obtained during the development of the ELUXYL™ Twin Raffinate process for the coproduction of PX and MX/OX mixture. In a first part, breakthrough experiments obtained for a xylene mixture with a particular adsorbent / desorbent couple are presented. It is shown that the selectivities of the different components are as follows : PX > EB > MX≈OX. Then, in a second part, results obtained on a SMB pilot plant operated with a second raffinate are stated. It is shown that by adjusting the ratio of the two raffinates

flowrates, it is possible to produce a mixture of meta- and orthoxylene isomers almost free of paraxylene and ethylbenzene in the second raffinate, with high purity PX being still recovered in the extract. In a last part, features about how to integrate this ELXUYL Twin Raffinate process in two process schemes to coproduce pure PX and either pure MX or OX are given.

Breakthrough experiments

When one looks at the development of an adsorption separation process, breakthrough experiments are an important part of the R&D work that has to be carried out. In fact, this type of experiments, with a suitable methodology of exploitation, allows to evaluate both thermodynamic and mass transfer data of the system.

Figure 1 displays a typical view of a breakthrough apparatus. This experimental system includes the following devices :

- two distribution networks (tank + pump + switch valve) : one for feed and one for desorbent. This enables to carry out breakthrough experiments (desorbent replaced by feed in the adsorbent column) or reverse breakthrough experiments (feed replaced by desorbent in the adsorbent column)
- one air bath where the adsorbent column is placed
- one cooler at the outlet of the heating system
- one fraction collector for chromatographic analysis

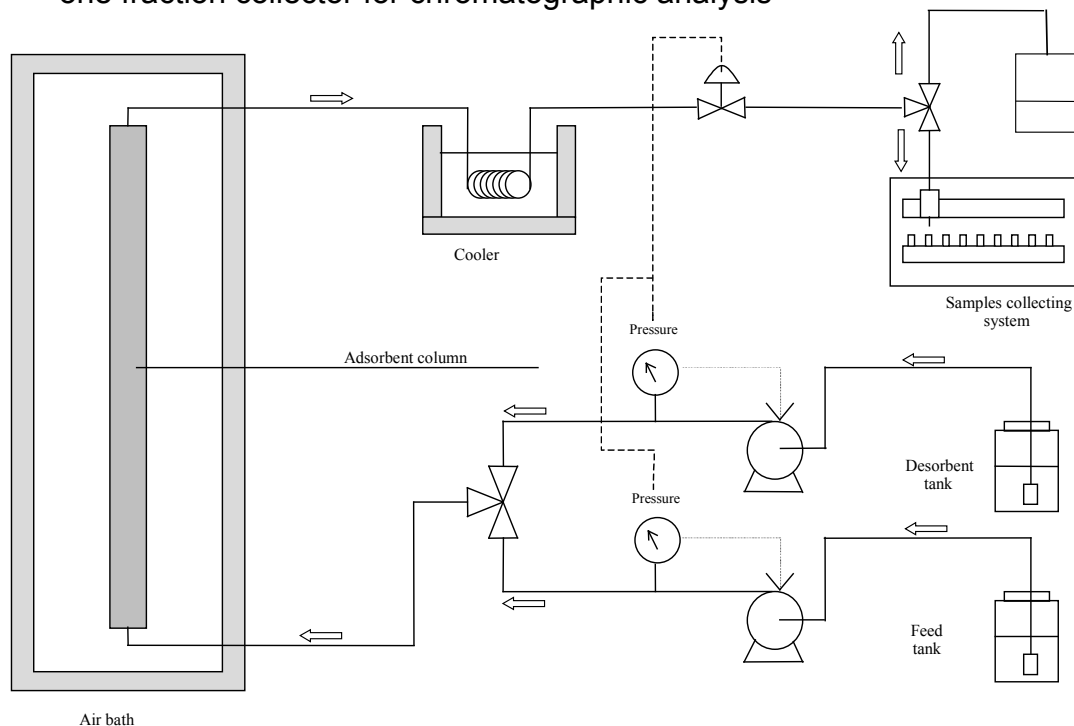


Figure 1 : Schematic view of an experimental breakthrough apparatus.

For a xylene mixture, which is our case of interest, we carried out a set of experimental breakthrough tests with different adsorbent / desorbent couples. One of them shows a particular behavior regarding the selectivities for the different components. These selectivities are in the following order : $PX > EB > MX \approx OX$ as it is

shown on figures 2.a and 2.b : indeed, it can be seen that EB breakthrough curve is intermediate between PX and MX curves.

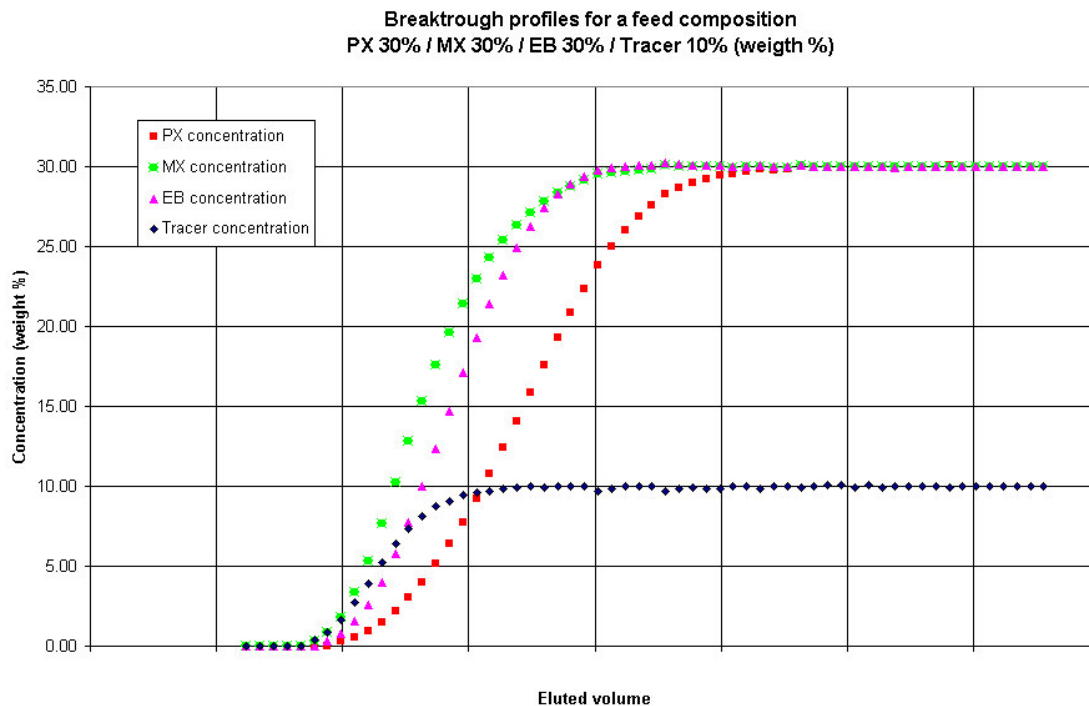


Figure 2.a : Breakthrough profiles for a xylene mixture of following mass composition : PX 30% / MX 30% / EB 30% / Tracer 10%.

An non-adsorbed tracer is used for non-selective volume evaluation. We observed that OX has the same behavior as MX regarding the selectivity. Therefore, OX was not specifically considered in our experiments.

Thermodynamic and mass transfer parameters were extracted from the set of experimental data (breakthrough + reverse breakthrough profiles). Those parameters were then implemented in a SMB process model to determine the operating parameters needed for the Twin Raffinate operation. This is going to be detailed in the next part.

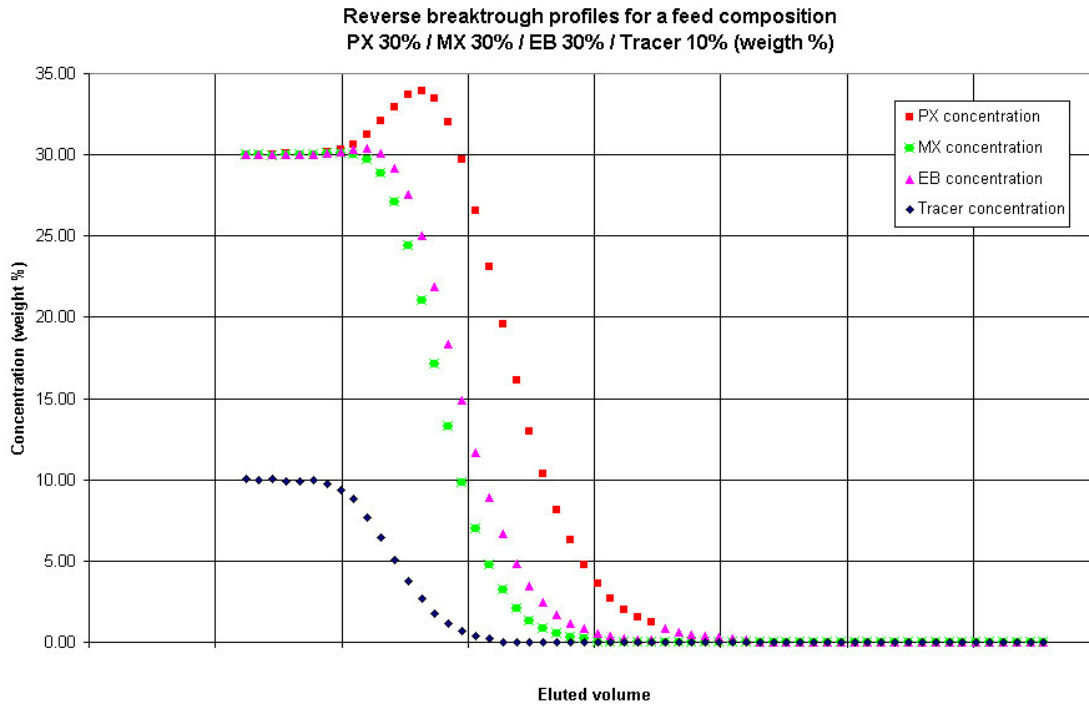


Figure 2.b : Reverse breakthrough profiles for a xylene mixture of following mass composition : PX 30% / MX 30% / EB 30% / Tracer 10%.

Simulation study, pilot plant tests and results analysis

Brief description of SMB Single and Twin Raffinate features

Before investigating the results obtained, we just remind a brief description of SMB process and we focus more particularly on the main features of the Twin Raffinate mode. In the case of paraxylene (PX) production, the conventional four zones SMB process allows to separate PX, which is recovered in the extract, from metaxylene (MX), orthoxylene (OX) and ethylbenzene (EB) which are withdrawn in the raffinate. More particularly, by adequately adjusting liquid flowrates in the different zones along with switching time value, the SMB process allows to produce PX with high purity and recovery. Figure 3.a displays a schematic configuration of a SMB Single Raffinate.

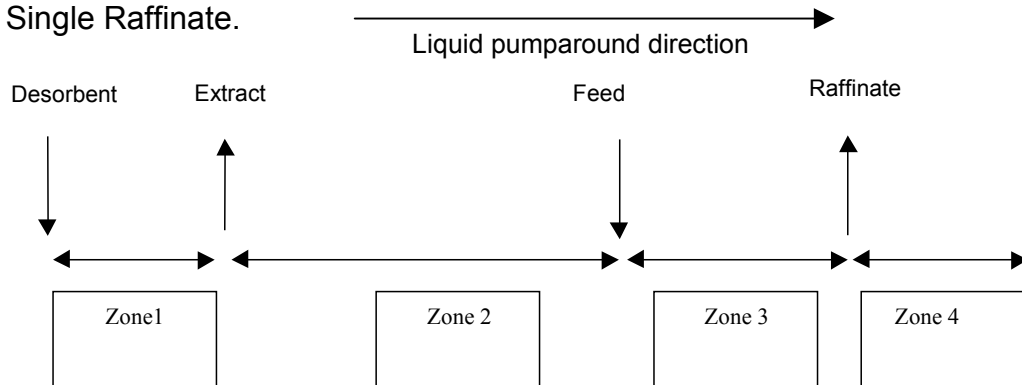


Figure 3.a : Typical SMB Single Raffinate configuration for PX separation.

As presented above, with a particular adsorbent / desorbent couple, the selectivity of the different components are as follows : $PX > EB > MX \approx OX$. Then, considering the case of a SMB operated with a second raffinate, the so-called Twin Raffinate mode, former zone 3 (located between the feed and the raffinate) is subdivided into two zones : zone 3A (from the feed to the first raffinate) and zone 3B (from the first raffinate to the second raffinate). By adequately adjusting the flowrate in zone 3B (for a given switching time), MX/OX mixture can be separated from EB. As shown below, the operating parameter for adjusting zone 3B flowrate is the ratio of raffinates flowrates $R2/R1$. Figure 3.b displays a schematic configuration of a SMB Twin Raffinate.

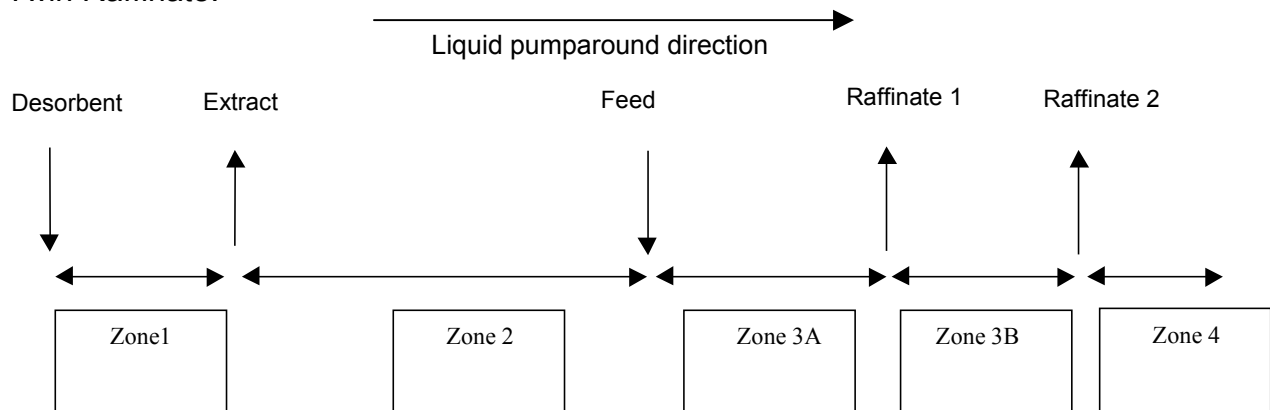


Figure 3.b : Typical SMB Twin Raffinate configuration for PX and MX/OX separation.

Simulation studies

Considering existing commercial PX units, the simulations and the experimentations shown below were carried out in order to evaluate the feasibility of adding an MX or an MX+OX coproduction in a limited revamp leading to keep 24 beds. For a new unit a different number of beds would be considered.

Simulations showed that the difference of selectivity between EB and MX/OX mixture allows a separation provided that correct configuration (number of beds) and flowrate of zone 3B are chosen. Different configurations were tested and flowrates were tuned to get a significant separation of MX/OX mixture from EB. Another aim was of course to keep PX purity and recovery equal to that of a conventional four zones SMB. It has been determined that :

- at least 3 beds are needed in zone 3B to get a noticeable separation between EB and MX/OX. Different configurations were tested, the total number of beds being 24, which is the number of beds classically used in a four zones SMB for PX separation. We thus were able to find out the optimum configuration for the Twin Raffinate operation.
- the ratio of flowrates of raffinate 2 to raffinate 1 ($R2/R1$) has to be in the range [0.4 - 0.7] to get interesting MX and OX purity and recovery.

Taking into account those simulation results, we performed pilot plant tests within the range of operating parameters of interest for coproduction of PX and MX/OX mixture.

Pilot plant tests : results and discussion

A series of pilot tests were carried out in order to validate the simulation studies made earlier. MX/OX purity and recovery that could be reached while maintaining PX purity and recovery at the level of the conventional ELUXYL™ process (purity > 99.8% and recovery > 97%) were evaluated.

On figure 4, a general view of the pilot plant and a detailed view of the on / off valves system for injections and withdrawals are displayed.



Figure 4 : general view of the pilot plant and a detailed view of the on / off valves system.

Pilot plant was operated in 24 columns mode, with a total volume of adsorbent of 9.1 L. The operating temperature and pressure were respectively 175°C and 10 bars.

On figure 5, the effect of R2/R1 ratio on the experimental concentration profiles within the unit is presented. For the three profiles, in order to physically illustrate what is happening in a Twin Raffinate SMB unit, only R1 and R2 flowrates were varied keeping constant all the other flowrates. For a given R2+R1 total flowrate, R2 was increased (decreasing R1 of the same amount). Doing so, zone 3B flowrate increases so that MX and OX profiles are displaced towards raffinate 2, while EB remains almost completely recovered in raffinate 1. Table 1 gives the detailed operating conditions in terms of flowrates and switching time for the three profiles presented below.

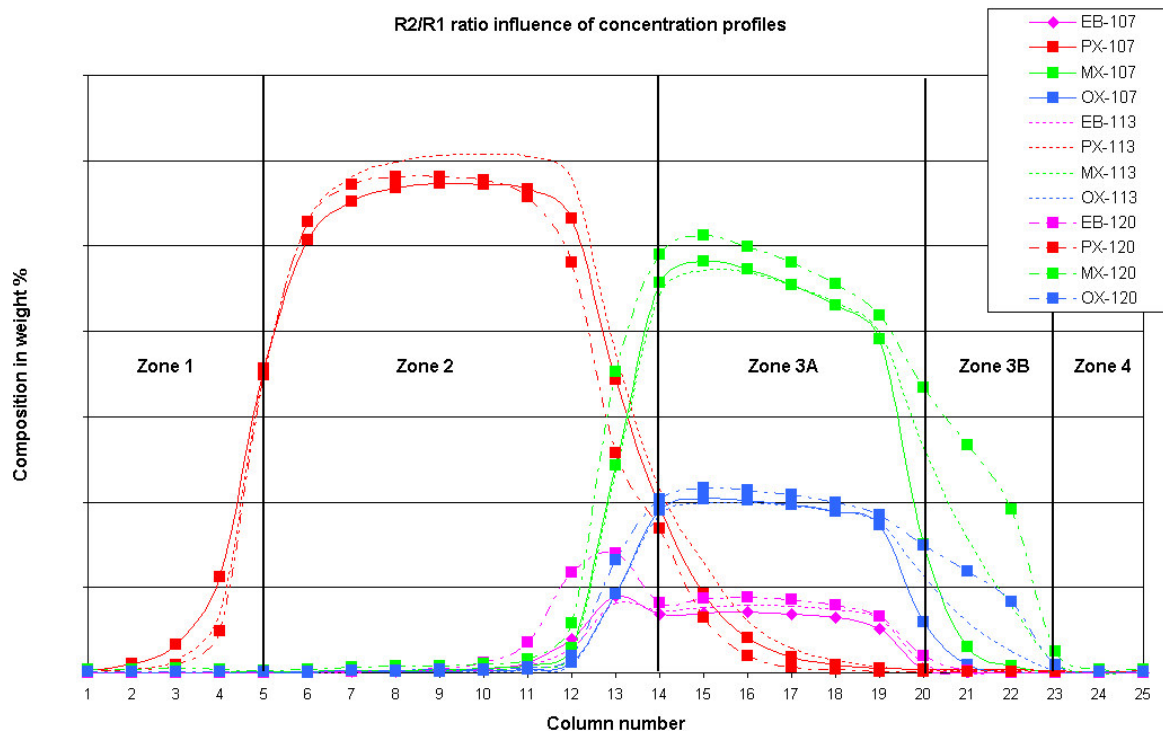


Figure 5 : Influence of R2/R1 operating parameter on the components profiles : profile 107 was obtained with R2/R1 = 0.07, profile 113 was obtained with R2/R1 = 0.21, profile 120 was obtained with R2/R1 = 0.44. All the other operating parameters were kept constants (see table 1 below). The configuration (number of beds per zone) is 4-9-6-3-2.

| | Profile 107 | Profile 113 | Profile 120 |
|--------------------|---------------|---------------|---------------|
| Desorbent | 91.71 | 91.73 | 91.84 |
| Extract | 53.37 | 53.42 | 53.20 |
| Feed | 54.12 | 54.24 | 54.24 |
| Raffinate 1 | 86.41 | 75.58 | 64.00 |
| Raffinate 2 | 6.05 | 16.97 | 28.88 |
| Zone 1 | 274.08 | 274.02 | 273.95 |
| Zone 2 | 220.71 | 220.60 | 220.75 |
| Zone 3A | 274.83 | 274.84 | 274.99 |
| Zone 3B | 188.42 | 199.26 | 210.99 |
| Zone 4 | 182.37 | 182.29 | 182.11 |
| Switching time | 70.80 | 70.80 | 70.80 |

Table 1 : Operating flowrates for the 3 profiles shown on graph 1. All flowrates are in cm³/min, switching time is in sec.

On figure 6, the evolution of PX, EB and MX+OX concentrations within raffinate 2 as a function of R2/R1 are presented. It can be first seen that the overall C₈-aromatics (i.e. PX+EB+MX+OX) concentration increases with R2/R1 ratio. This is due to a decrease in desorbent concentration in raffinate 2. This decrease can be attributed to the move of the MX and OX, and in a lesser extent EB profiles towards

raffinate 2, which is clearly illustrated on figure 5 where MX and OX concentrations in zone 3B increase.

When R2/R1 becomes greater than 0.4-0.5, there is a radical change of the slope of EB concentration while MX/OX concentration tends to reach a maximal value, thus resulting in a limitation of MX/OX purity. This slope increase is due to the start of EB breakthrough in zone 3B. For values of R2/R1 ratio higher than 0.65, MX/OX purity would start to decrease as :

- EB concentration would still increase until the complete breakthrough of EB profile in raffinate 2.
- MX and OX concentrations would remain almost constant at a value equal to that of the plateau found for the two isomers in zone 3A.

Concerning PX concentration in raffinate 2, it has to be underlined that whatever the value of R2/R1, PX content remains at a relatively constant level ranging in the 0.05-0.1% order of magnitude.

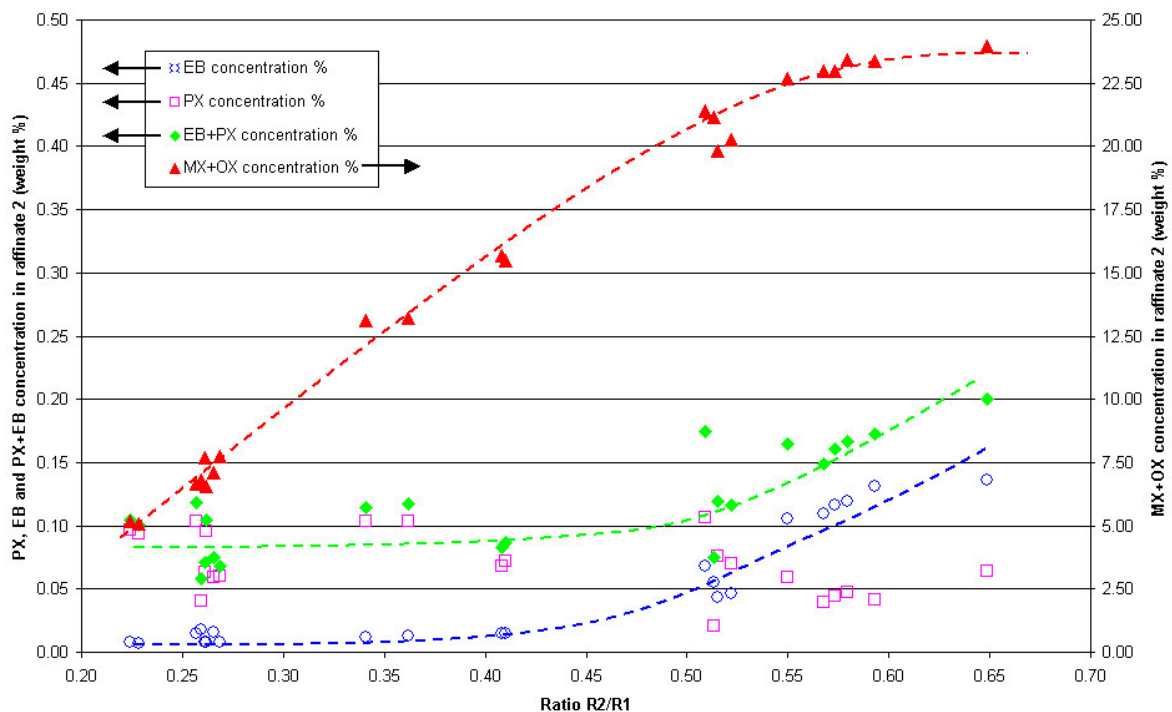


Figure 6 : PX, EB, PX+EB and MX+OX concentrations in raffinate 2 as a function of R2/R1 ratio.

In order to evaluate the performance of the Twin Raffinate ELUXYL™ process for both PX and MX/OX mixture production, the following calculations were used:

- For PX :

$$\text{PX purity} = \frac{\%PX_{\text{Ext}}}{\%PX_{\text{Ext}} + \%EB_{\text{Ext}} + \%MX_{\text{Ext}} + \%OX_{\text{Ext}}}$$

$$\text{PX recovery} = \frac{[PX]_{\text{Flowrate in Ext}}}{[PX]_{\text{Flowrate in Feed}}}$$

which are the classical formulation for PX purity and recovery.

- For MX/OX :

$$\text{MX/OX purity} = \frac{(\%MX + \%OX)_{R2}}{(\%MX + \%OX)_{R2} + \%EB_{R2} + \%PX_{R2}}$$

$$\text{MX/OX recovery} = \frac{[\text{MX} + \text{OX}]_{\text{Flowrate in R2}}}{[\text{MX} + \text{OX}]_{\text{Flowrate in Feed}}}$$

which gives a clear evaluation of both MX/OX recovery and raffinate 2 depletion in PX and EB (other trace components are not taken into account).

MX/OX purity and recovery as a function of R2/R1 ratio are reported in figure 7. It is interesting to notice that for R2/R1 varying from 0.22 to 0.65, MX/OX recovery is linearly increasing from 3.0% to almost 30% while MX/OX purity is increasing from 98.0% up to 99.3-99.4%. For all these runs, PX purity was greater than 99.8% and recovery ranged from 97.0% to 98.0%.

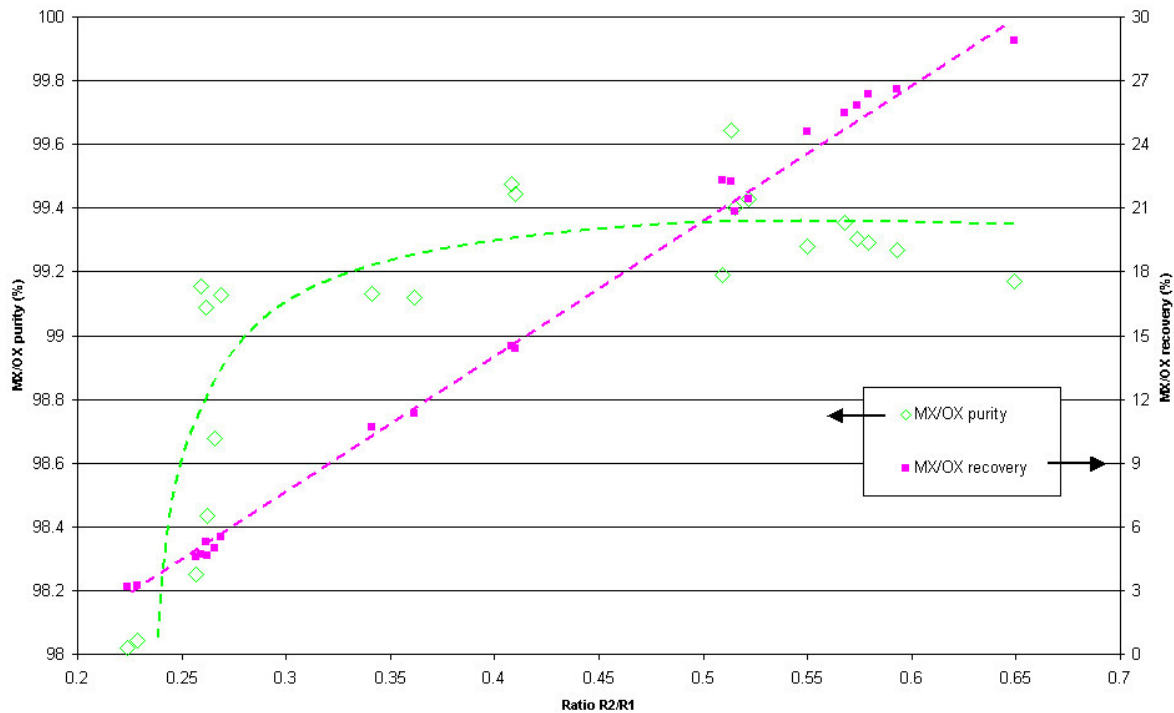


Figure 7 : MX/OX purity and recovery as a function of R2/R1 ratio.

The explanation for the 99.3-99.4% purity plateau that is reached for MX/OX purity for R2/R1 ratios greater than 0.4-0.5 is due to the linear increase of PX+EB concentrations while MX+OX concentration increases and tends to reach a maximal value as illustrated in figure 6.

Pilot plant tests : conclusion

Through the analysis of the pilot plant tests, it has been shown how to operate an ELUXYL™ Twin Raffinate process. More particularly, the evolution of MX/OX purity and recovery in raffinate 2 as a function of the key operating parameter R2/R1 were presented. In terms of performance, PX can be still recovered in extract with high purity and recovery (99.8%+ and 97%+) and a mixture of ortho- and metaxylene can be recovered in the second raffinate. MX/OX purity ranges from 98.0% up to 99.3-99.4%, while the recovery ranges from 3% up to 30% depending on R2/R1 value.

Therefore, the Twin Raffinate technology offers an interesting flexibility for the coproduction of PX and MX/OX mixture. Operation of this Twin Raffinate ELUXYL™ process is not more difficult than the conventional ELUXYL™ process. It is characterized only by the use of an additional operating parameter which is the ratio of the second raffinate flow rate to the first raffinate flow rate. The other regular operating parameters for paraxylene separation are still valid.

In the next part, it is shown how to take advantage of this operation for the coproduction of PX and either pure MX or OX.

Integration of ELUXYL™ Twin Raffinate into two process schemes

Pure MX is the petrochemical intermediate mainly used to produce purified isophthalic acid (PIA) which is then used for the production of modified PET (PolyEthyleneTerephthalate). As the market demand for that form of PET increases, there is an increasing need for producing pure MX.

Concerning OX, it is mainly used to produce phthalic anhydride, a base chemical used in plasticizers and painting industry.

In order to produce pure MX (and possibly pure OX) along with PX, two interesting process schemes were investigated. They are presented in table 2 (Leflaive et al., 2003), (Leflaive et al., 2002). Figures 8.a and 8.b give more details about those two processes.

| | |
|-------------------------|-------------------------|
| • Process integration A | • Process integration B |
| ELUXYL™ Twin Raffinate | ELUXYL™ Twin Raffinate |
| MX/OX splitter | MX SMB unit |
| Crystallization unit | |

Table 2 : General description of process integrations A and B.

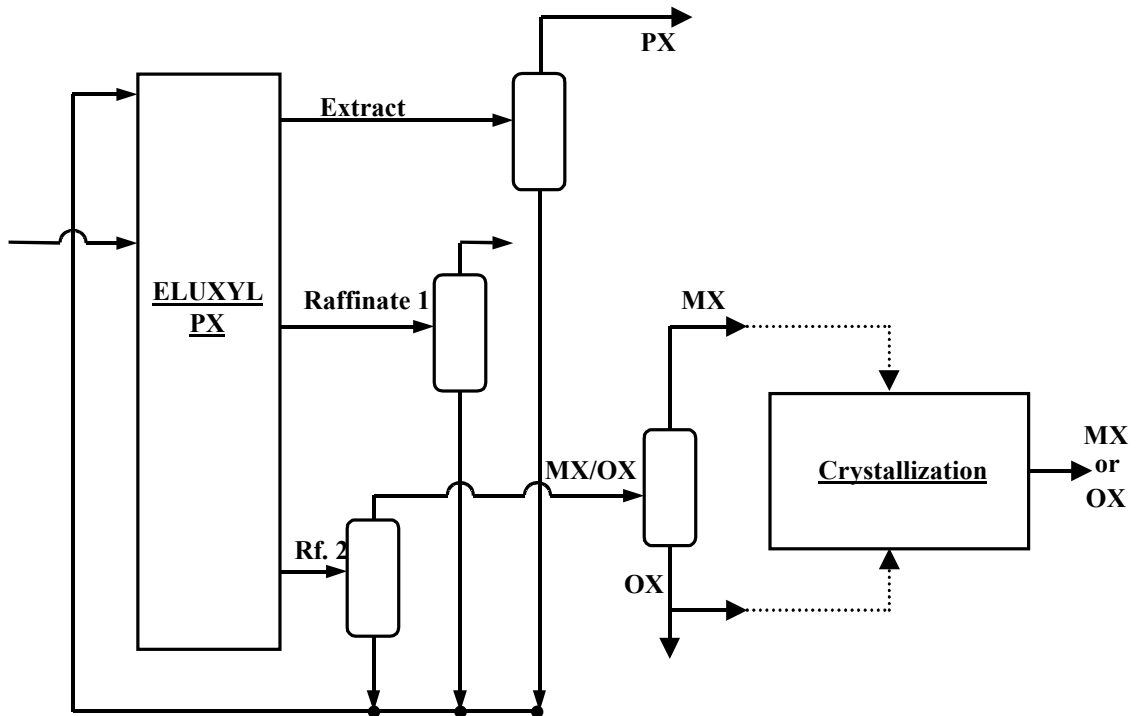


Figure 8.a : Schematic view of process integration A : ELUXYL™ Twin Raffinate + MX/OX splitter + Crystallization.

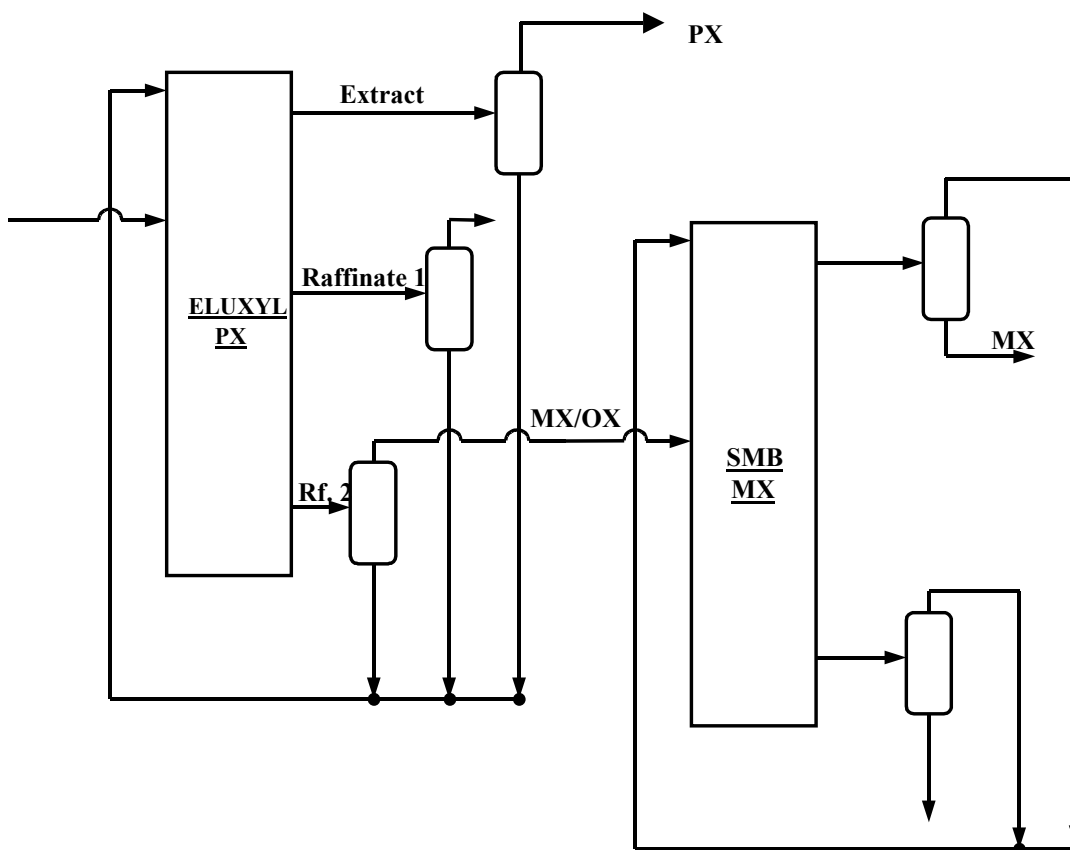


Figure 8.b : Schematic view of process integration B : ELUXYL™ Twin Raffinate + MX SMB unit.

In process integration A, raffinate 2 coming from the ELUXYL™ Twin Raffinate is sent to an MX/OX splitter. Then, either the head or the bottom stream is sent to a crystallizer for production of MX or OX respectively (see figure 8.a). Therefore, the interesting point of this process scheme is the flexibility offered for either producing MX or OX. The main parameter is the composition of the stream sent to the crystallization unit from the splitter. Indeed, depending on which isomer one wants to produce, the composition has to be in the right part of the MX/OX binary solid - liquid equilibrium diagram (see figure 9). One should notice that the very low EB and PX concentrations of raffinate 2 will not affect the binary equilibrium. Therefore for MX crystallization, the composition of the head product should be located in the region delimited by pure MX point, MX/OX binary eutectic point and the liquidus line. For OX crystallization, the composition of the bottom product should be located in the region delimited by pure OX point, MX/OX binary eutectic point and the liquidus line.

Considering process integration B (see figure 8.b), the main aspect is that it is especially dedicated to MX production. Raffinate 2 coming from the ELUXYL™ Twin Raffinate is sent to another SMB unit dedicated to the production of MX at high purity (99.5+%) and high recovery. It can be noted that raffinate 2 is a better feed for the second SMB unit than a conventional single raffinate stream, as it is more concentrated in MX and as it is completely depleted in EB. The use of ELUXYL™ Twin Raffinate technology process integration B allows then to reduce the amount of adsorbent and desorbent needed in MX SMB unit, which leads to important savings in both investment and operational costs for MX coproduction.

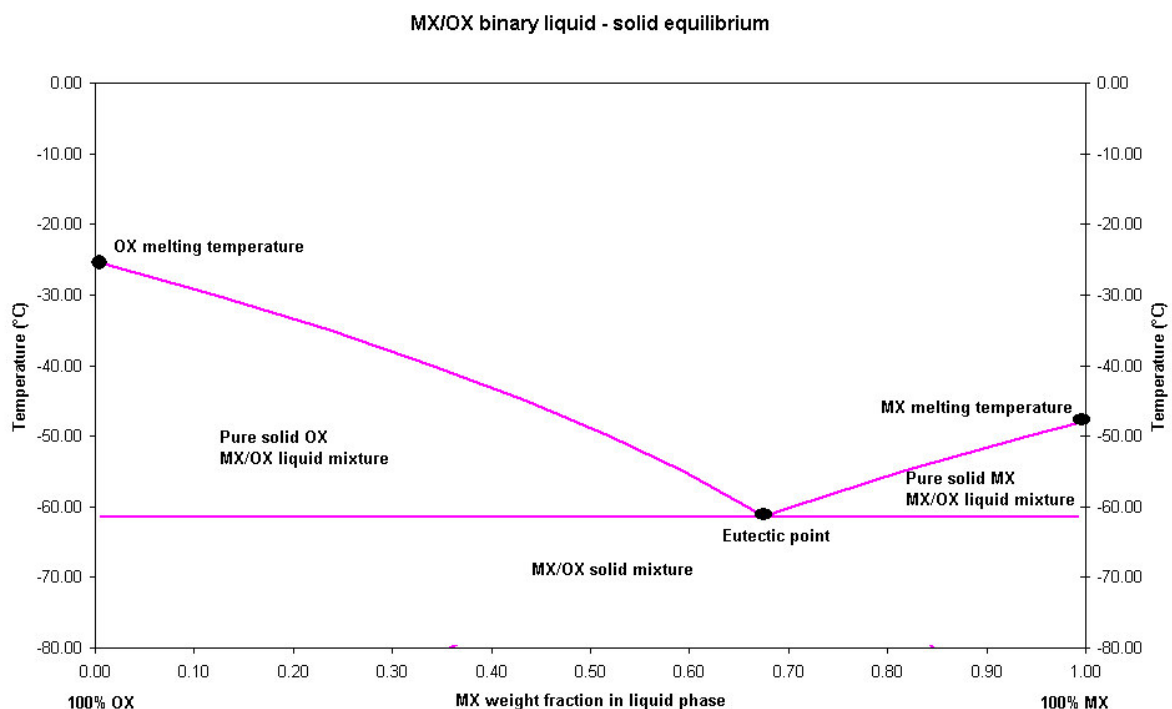


Figure 9 : Binary MX/OX solid - liquid equilibrium diagram.

Conclusion

In this paper, the results of the development of the ELUXYL™ Twin Raffinate technology are presented.

In a first step, breakthrough experiments were carried out, enabling the determination of an interesting adsorbent / desorbent couple. The selected couple exhibits selectivities in the following order : $PX > EB > MX \approx OX$. Simulations showed how this behavior could be smartly used in a Twin Raffinate SMB process and pilot plant tests confirmed that both pure PX and a MX/OX mixture depleted in PX and EB could be obtained in a 24 beds Twin Raffinate SMB unit. In terms of performances, a mixture of MX/OX can be produced with a 99.3-99.4% purity and a recovery ranging from 15% to almost 30% for R2/R1 ranging from 0.4 to 0.6. Those results were obtained at a PX purity and recovery equal to that of a conventional four zones SMB (99.8%+ and 97%+).

Therefore, the Twin Raffinate technology offers an interesting flexibility for the coproduction of PX and MX/OX mixture. Operation of this Twin Raffinate ELUXYL™ process is not more difficult than the conventional ELUXYL™ process. It is characterized only by the use of an additional operating parameter which is the ratio of the second raffinate flow rate to the first raffinate flow rate. The other regular operating parameters for paraxylene separation are still valid. From the engineering point of view, in the ELUXYL™ process, injection and withdrawal of products are operated by a robust independent on-off valves system. Therefore, the conventional ELUXYL™ process would be easily adapted for the withdrawal of a second raffinate by the implementation of a new valves set (24 more valves than a conventional Stand Alone ELUXYL™ process).

Finally, it is presented how it can be taken advantage of the Twin Raffinate operation for the coproduction of PX and either pure MX or OX. Two options are given for the integration of the ELUXYL™ Twin Raffinate. The first one comprises a splitter plus a crystallizer unit that allows coproduction of either MX or OX. The second one is dedicated to MX production using a specific SMB unit for MX separation downstream the ELUXYL™ Twin Raffinate process.

To conclude, ELUXYL™ Twin Raffinate Technology offers an interesting flexibility to coproduce PX and either MX or OX depending on which integration scheme is chosen downstream.

The rapid and successful development of the ELUXYL™ Twin Raffinate technology, clearly shows that IFP and AXENS can rapidly bring both smart solutions to respond to market needs and competitive technological evolutions of the conventional processes.

The efficient and well-tried methodology used, combined with in-depth technical skills of IFP multidisciplinary expert teams, allowed to rapidly come from lab-scale experiments up to industrial applications.

The methodology included :

- Adsorbent studies: Using thermogravimetric, pulse and breakthrough experiments, both thermodynamic and mass transfer data of the adsorbent / desorbent system could be extracted. These experiments, combined with adsorbent formulation specialists know-how, were of great use to get a complete understanding of the physico-chemical phenomena that occur within the adsorbent and in further optimizing the adsorbent / desorbent system design.

- Simulation studies : using different kinds of models, Process Technology Group was able, in a first step, to target the optimal range of operating parameters thus allowing to reduce the pilot plant tests duration and consequently the total duration of process development. In a second step, once pilot plant tests were obtained, the detailed process model was finely tuned on experimental data to help industrial process start-up and operating parameters optimization.
- Pilot plant tests : these experiments could validate simulation results, evaluate performance and optimize operating parameters in industrial conditions (temperature, liquid velocity, industrial adsorbent and feed, ...).

The developed methodology, based on the sharing of the knowledge throughout the organization, gives the IFP the ability of resolving both technology and operational issues for the separation technology. This, in turn, brings AXENS a useful support in the analysis, development and implementation of key industrial projects, both revamp and new projects, aiming at a feasible balance between cost-efficiency and downstream equipment safety or product quality.

References

Ash G, Barth K, Hotier G, "ELUXYL - A new paraxylene separation process", Revue de l'Institut Français du Pétrole, 49(5), p 541-549, 1994

Hotier G., MacPherson S., Weber R., Renard P., "Para-xylene production : Integrating modern technological solutions into an existing complex", Proceedings of the 16th World Petroleum Congress, 4, p 173-183, 2000

Hotier G., Méthivier A., "Debottlenecking of Existing Aromatic Production Loop : The Hybrid Eluxyl Process Offers An Attractive Alternative Solution", Proceedings of the AIChE Spring Meeting, paper reference 122d, 2002

Leflaive P., Methivier, A., Hotier, G., "Process for co-producing para-xylene and metaxylene, comprising two separation steps", US20020143223 A1

Leflaive P., Wolff L., Hotier, G., Methivier, A., "Process for co-production of paraxylene, metaxylene and/or orthoxylene", US20030069461A1