

## SEPARATION OF METHANOL/BUTENE/MTBE USING HYBRID DISTILLATION-MEMBRANE PROCESSES

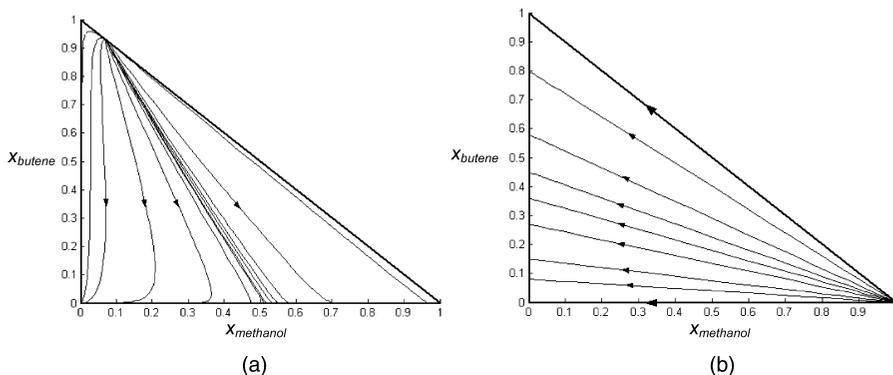
Mark Peters, Shehzaad Kauchali, Diane Hildebrandt, David Glasser  
Centre of Materials and Process Synthesis, School of Chemical and Metallurgical Engineering,  
University of the Witwatersrand, Private Bag 3, WITS 2050, Johannesburg, South Africa;  
E-mails: mpeters@prme.wits.ac.za; shehzaad.kauchali@comps.wits.ac.za;  
dihil@comps.wits.ac.za; david.glasser@comps.wits.ac.za

Distillation Residue Curve Maps (D-RCM's) have proven to be an extremely useful graphical tool in the design and operation of both batch and continuous distillation processes. Recently submitted work by the authors has investigated the applications of Residue Curve Maps for membrane permeation systems. Such maps are referred to as M-RCM's. This paper aims to develop a graphical tool to provide insight in sequencing combinations of unit processes in complex systems. As an example, the separation of a methanol/butene/MTBE system is investigated. MTBE is the desired product, and hence needs to be efficiently recovered from a reactor product. Difficulty arises when separating such a mixture with traditional distillation processes, because of the binary azeotropes that exist between methanol and MTBE, as well as methanol and butene. A membrane is suited for such a separation since it is not limited by relative volatility constraints. Using available data for the permeation rates of the components through a chosen membrane, the M-RCM was plotted. The M-RCM, along with column profile maps, facilitated a graphical method to select a combination of profiles to obtain the desired product(s). The method displayed can be applied to the design, as well as extended to the synthesis of hybrid processes. Maintaining an appropriate permeate pressure, it was found that crossing the distillation boundary is possible!

KEYWORDS: distillation, membranes, residue curve maps, separation, graphical, hybrid, design

### INTRODUCTION AND LITERATURE REVIEW

Methyl tertiary-Butyl Ether (MTBE) is a fuel additive. Its demand has increased due to an environmental drive to phase-out lead-compound emissions in fuels. MTBE is produced industrially by the reaction between methanol and *i*-butene. *i*-Butene arises from a cracking plant, and arrives at the reactor as part of a C<sub>4</sub> hydrocarbon stream. For simplicity, it is assumed that the C<sub>4</sub> stream contains only *i*-butene and 1-butene. The reaction is equilibrium limited, and in order to obtain high conversions of *i*-butene, methanol is fed in excess (Rehfinger and Hoffmann, 1990). It can further be assumed that the ratio of methanol to *i*-butene is such that all the *i*-butene is converted. The reactor product, therefore, consists of recently formed MTBE, unconverted methanol as well as 1-butene.



**Figure 1.** (a) D-RCM at  $P = 6\text{ bar}$ . (b) M-RCM for a vacuum permeate pressure

The reactor product needs to be efficiently separated. Figure 1(a) shows the Distillation Residue Curve Map (D-RCM) for the system. In the traditional Hüls process (Bausa and Marquardt, 2000), a two-column sequence is used. The first column operates at a pressure of 6bar. The distillate composition is nearly that of the butene/methanol azeotrope. This stream is sent back to the cracking plant from where the C4 stream originated. The bottoms is sent to the second column where pure MTBE is produced, as well as an azeotropic mixture of methanol and MTBE. To avoid too much MTBE reporting to the azeotropic mixture, the pressure in the second column is increased to about 12bar. The MTBE is the required product, while the methanol (containing MTBE) is recycled back to the reactor.

In an attempt to recover more of the MTBE that is produced in the reactor, a membrane could be used to facilitate the separation. Various membranes have been developed for such a separation (Bangxiao et al., 2001; Bausa and Marquardt, 2000; Hommerich and Rautenbach, 1998; Lu et al., 2002).

This paper focuses on the use of a distillation-membrane hybrid as an alternative to the Hüls process. Such an alternative is not something new, but has been researched before (Bausa and Marquardt, 2000; Hommerich and Rautenbach, 1998; Lu et al., 2002). What we propose in this paper is simply a novel graphical method of designing such systems. Lu et al. (2002) manage to design a hybrid process using rigorous mathematical calculations, but their method does not enable them to examine other configurations. Hommerich and Rautenbach (1998) examine the feasibility of various process configurations. They design each of these using ASPEN PLUS<sup>®</sup> with a FORTRAN subroutine for the membrane unit. Their optimization techniques however are somewhat trial-and-error. Bausa and Marquardt (2000) utilize shortcut methods for design of both the distillation and membrane units. This enables them to design the hybrid process graphically. However, the reflux and/or reboil ratios, as well as the number of theoretical trays

needed are not so easily accessible. They do furnish the reader with a method to obtain the minimum membrane area required.

In order to formulate a graphical technique for designing hybrid systems, Membrane Residue Curve Maps (M-RCM's) were developed Peters et al. (2006). These maps were developed in much the same manner as D-RCM's. The resulting equations, in fact, were shown to be identical to those used in plotting a D-RCM. Using appropriate flux equations to model the permeate phase as a function of the retentate composition, one is able to plot such a map. The plot shows the compositional change of the retentate as permeation proceeds. PERVAP 1137 is a membrane manufactured by Sulzer Chemtech® that is selective to methanol permeation. Bausa and Marquardt (2000) give flux model data for this particular membrane. Using this data, the M-RCM was plotted, as shown in Figure 1(b).

The membrane can not be used as a stand alone unit to produce the required products, since it is possible to only obtain a pure methanol stream (refer to Figure 1(b)). Hence needs to be used in conjunction with a distillation column. Unlike distillation, the membrane is not dependant on relative volatilities, and hence the distillation boundary can be crossed. Furthermore, the functioning of the membrane is highly dependant on the permeate pressure Peters et al. (2006), and needs to be taken into consideration. It has previously been shown how the map changes with various permeate pressures. For the hybrid design described here, it will be assumed that the permeate pressure is sufficiently close to vacuum.

## DESIGN REQUIREMENTS

The required products from the hybrid separation are:

- An essentially pure MTBE stream,
- A pure methanol stream, which will be recycled back to the reactor, and
- A butene-rich stream, which will be returned back to the plant from which it originated.

Table 1 shows the compositions of the feed and product streams.

**Table 1.** Steam composition

Stream	Composition [methanol, butene, MTBE]
Feed (F)	[0.45, 0.09, 0.46]
Distillate (D)	[0.07, 0.925, 0.005]
Permeate (P)	[1, 0, 0]
Bottoms (B)	[0.001, $10^{-7}$ , 0.998999]

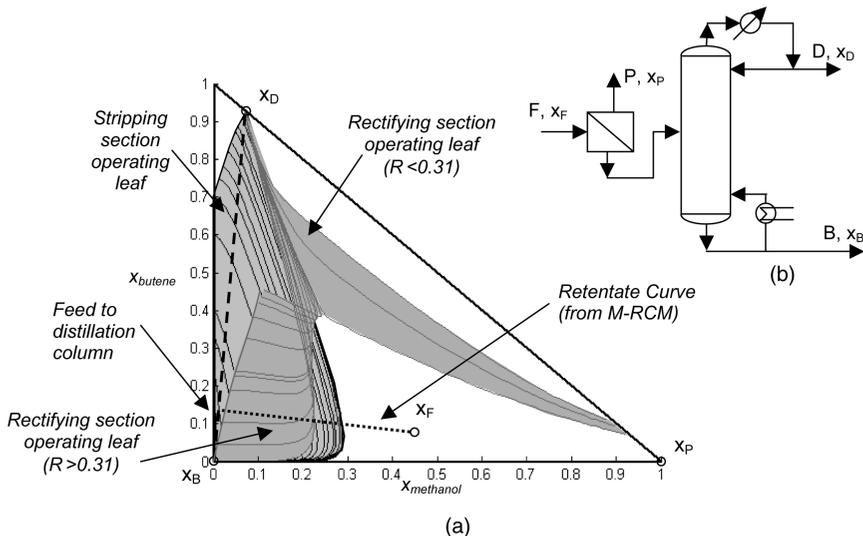
## HYBRID DESIGNS

There are many configurations for hybrid systems that can be explored: placing the membrane upstream from the column, or placing it downstream. One could also side-connect the membrane to the column in various ways. In this paper, we will now look at two particular configurations. In the first, an example of how one can *synthesize* a configuration is discussed. In the second, a system is chosen and the details of the method of *design* are given.

### MEMBRANE UPSTREAM OF COLUMN

On the D-RCM (refer to Figure 1(a)), MTBE has the highest boiling point, and would thus, traditionally, be expected to be the bottoms product of distillation column, irrespective of membrane placement. Using this, one could generate the operating leaf (Castillo et al. (1998)) for the required MTBE product composition. Similarly, the methanol/butene azeotrope is the lowest boiling point on the D-RCM, and would more than likely be the distillate. The operating leaves for both the rectifying and stripping sections have been superimposed and are shown in Figure 2(a).

One can see that a bifurcation occurs within the rectifying leaf, resulting in an “open” leaf. This occurs at a reflux of about 0.31. Furthermore, and more importantly, there is a definite overlap of the two leaves, indicating that a standard single feed, two



**Figure 2.** (a) Operating leaves for distillate and bottoms products, and membrane profile for the (b) process configuration

product column is feasible. A further requirement for such a column to be practical is that the feed composition (to the column) has to lie on the straight line connecting  $x_D$  and  $x_B$ , by material balance. The overall feed (from the reactor), however, does not obey this requirement (refer to Figure 2(a)).

A membrane can be used before the column in order to move the overall feed to a point on the straight line connecting  $x_D$  and  $x_B$ . The membrane will deplete the feed of most of its methanol. The M-RCM shows the exact path the retentate will follow from feed composition to the desired composition of the distillation feed, as shown in Figure 2(a). Figure 2(b) shows the synthesized process configuration.

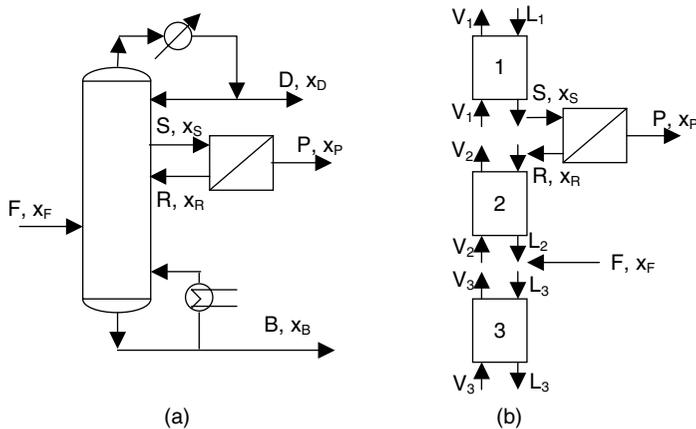
Once the distillation feed is obtained, the design of the column proceeds using “traditional” methods. The actual choice of reboil/reflux ratio(s) depends on an optimization process, which is out of the scope of this particular report, but will be discussed in a future publication.

### MEMBRANE SIDE-CONNECTED TO THE COLUMN

The configuration discussed in Section 3.1 above was synthesized, rather than designed. In this option, a particular chosen sequence of units is designed.

Consider the hybrid configuration shown in Figure 3(a).

The MTBE, having the highest boiling point, will report to the bottom of the column. At 6bar, the highest concentration of butene obtainable, without losing too much MTBE would be the binary methanol/butene azeotrope (refer to Figure 1(a)). The azeotrope has the lowest boiling point on the map, and will be removed at the top of the column. The methanol will be a product of the membrane.



**Figure 3.** (a) A possible hybrid configuration, (b) the column sections for the hybrid system

This process shown in Figure 3(a) can be broken up into the column sections (Tapp et al., 2004), as shown in Figure 3(b). Each column section (1–3) has its own unique profile. The difference point equation (DPE) describing a column profile is (the constant molar overflow assumption is employed):

$$\frac{dx}{dn} = \left( \frac{1}{R_{\Delta}} + 1 \right) (x - y^*) + \frac{1}{R_{\Delta}} (X_{\Delta} - x) \quad (1)$$

with

$$X_{\Delta} = \frac{V \cdot y_T - L \cdot x_T}{\Delta}; \quad R_{\Delta} = \frac{L}{\Delta} \quad \text{and} \quad \Delta = V - L \quad (2)$$

where  $x$  is the liquid composition

$n$  is the number of theoretical stages

$y^*$  is the vapour in equilibrium with  $x$

$X_{\Delta}$  is the difference point

$V$  is the molar vapour flowrate in a column section [mol/s]

$L$  is the molar liquid flowrate in a column section [mol/s]

$R_{\Delta}$  is the reflux ratio

$\Delta$  is the net molar flow in a section [mol/s]

$x_T$  and  $y_T$  are the molar liquid and vapour compositions at the top of a column section

The profile for each of the sections depends on the  $X_{\Delta}$ - and  $R_{\Delta}$ -values for that particular section. It is worth noting that should the constant molar assumption be relaxed, equation (1) still holds true since it is merely a differential material balance across a column section. One can prove this result, but it is not given here since it is out of the scope of this report. Holland et al. (2004) show that any distillation configuration, no matter how complex, can be modeled using column profile maps (CPM). The method described below is an extension of the work put forward by Holland et al. (2004). While Holland et al. (2004) focused on distillation only, we include the addition of a membrane unit linked to column sections.

#### Method of design

- On the map(s), locate feed point
- Identify and plot compositions of product streams
- Perform overall and component material balance across the *entire* system:

$$F = D + P + B \quad \text{and} \quad Fx_F = Dx_D + Px_P + Bx_B \quad (3)$$

This will allow one to establish the product flowrates for a specified feed.

The method will follow a “bottom-up” calculation, commencing with section 3, and ending at section 1.

*Section 3:*

- In section 3, material is being removed at the end of the section:

$$\Delta_3 = V_3 - L_3 = -B \quad (4)$$

meaning that the net flow of material in section 3 is downward.

- Plot the column profile for section 3 using  $x_B$  and various  $R_{\Delta 3}$ -values. The stripping section operating leaf shown in Figure 2(a) shows various profiles for this section.
- An appropriate  $R_{\Delta 3}$ -value must be chosen, remembering that it is negative in sign. Figure 4(a) shows the section profile at a selected  $R_{\Delta 3}$ -value.

*Section 2:*

- Calculate  $X_{\Delta 2}$  using the material balances around the feed point:

$$F = \Delta_2 + B \quad \text{and} \quad Fx_F = \Delta_2 X_{\Delta 2} + Bx_B \quad (5)$$

This implies that  $x_F$  must lie on the straight line between  $X_{\Delta 2}$  and  $x_B$ .

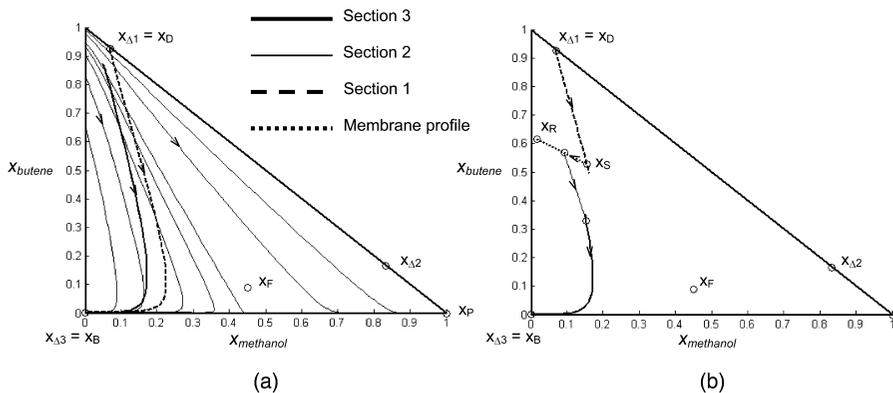
- Calculate  $R_{\Delta 2}$  by mass balance across the feed, assuming the feed is all liquid.
- Produce an entire CPM using  $X_{\Delta 2}$  and  $R_{\Delta 2}$  – use this map to select candidate profiles, when necessary (see later). This map is shown in Figure 4(a).

*Section 1:*

- The mass balance around the membrane side-draw and return is:

$$\Delta_2 = D + P \quad \text{and} \quad \Delta_2 X_{\Delta 2} = Dx_D + Px_P \quad (6)$$

implying that  $x_{\Delta 2}$  must lie on the straight line between  $x_D$  and  $x_P$ .



**Figure 4.** Profile maps for the various column sections (refer to Figure 3(b)) and the membrane unit

- Determine  $R_{\Delta 1}$  using equation (6)
- $X_{\Delta 1}$  is fixed – it is the distillate composition,  $x_D$ .
- Plot column profile for section 1, as shown in Figure 4(a)

*Putting it all together...*

- Now, starting at the distillate composition, follow the profile for section 1. It is the designer's choice where to end this section. But it should be remembered that numerous stages are needed for a profile to “go around the corner” as a profile approaches a saddle node. It is therefore assumed that section 1 should be terminated well before any corners!
- Using section 1's exit liquid composition as the feed to membrane, perform the mass balance to ensure that the retentate composition lies within the MBT. If this is not the case, then one needs to re-set the value for  $R_{\Delta 3}$ .
- Also remember that not all the liquid leaving section 1 is fed to the membrane, and that the retentate is then mixed with the remaining liquid to give the liquid entering the top of section 2.
- Follow the profile for section 2, ensuring that it intersects with section 3 at composition within the MBT. If this is not the case, then the designer needs to re-evaluate the termination point of section 1.
- It is necessary to note the *direction* of the profiles. The configuration is not feasible if the directions of each of profiles do not match the order of the sections.

Using the above method, a design was arranged. Figure 4(b) shows where the profiles for each section commence and terminate. It is worth noting that this design is, by no means, necessarily the optimal design for the chosen hybrid configuration.

### CLOSING REMARKS

In this article, it has been shown that using both D- and M-RCM's it is possible to graphically interpret hybrid distillation/membrane processes. It has been revealed how one can synthesize a configuration for a particular separation, as well as design a given arrangement. The methods, while being trial-and error, utilize a graphical technique making this method novel: With the use of column profiles, it is possible to retrieve data such as the reflux/reboil ratio as well as the theoretical number of stages needed in each section. Furthermore, using the M-RCM, it is possible to obtain the required membrane area to achieve the necessary separation. This approach of designing hybrid systems can be extended to many configurations, which can ultimately be screened by an optimization technique. It should be obvious that the sequencing of the separation units in a hybrid process is such that each unit operates in the region of the composition space where its separation ability is best suited and most effective.

This article only highlights two possible configurations, and does not by any means attempt to optimally design each. Additionally, an overall optimum design is not sought, since it is out the scope this particular article. Future publications from the authors will give detailed methods of optimization techniques that can be employed.

**NOMENCLATURE****SYMBOLS**

$B$	Bottoms [mol/s]
$D$	Distillate [mol/s]
$\Delta$	Net molar flow in a section [mol/s]
$F$	Feed [mol/s]
$L$	Molar liquid flowrate in a column section [mol/s]
$n$	Number of stages [-]
$P$	Permeate [mol/s]
$R$	Retentate [mol/s]
$R_{\Delta}$	Reflux ratio [-]
$S$	Side-draw [mol/s]
$V$	Molar vapour flowrate in a column section [mol/s]
$x$	Liquid composition [-]
$x_T$	Molar liquid composition at the top of a column section [-]
$X_{\Delta}$	Difference point [-]
$y^*$	Vapour in equilibrium with $x$ [-]
$y_T$	Molar vapour composition at the top of a column section [-]

**ABBREVIATIONS**

CPM	Column Profile Map
DPE	Difference Point Equation
D-RCM	Distillation Residue Curve Map
MBT	Mass Balance Triangle
M-RCM	Membrane Residue Curve Map
MTBE	Methyl tertiary Butyl Ether

**REFERENCES**

- Bangxiao, C., Lu, Y., Hailin, Y. & Congjie, G. (2001). Effect of separating layer in pervaporation composite membrane for MTBE/MeOH separation. *Journal of Membrane Science*, 194, 151–156.
- Bausa, J. & Marquardt, W. (2000). Shortcut Design Methods for Hybrid Membrane/Distillation Process for the Separation of Nonideal Multicomponent Mixtures. *Industrial and Engineering Chemistry Research*, 39, 1658–1672.
- Castillo, F. J. L., Thong, D. Y. -C. & Towler, G. P. (1998). Homogeneous Azeotropic Distillation. 1. Design procedure for single-feed columns at nontotal reflux. *Industrial and Engineering Chemistry Research*, 37, 987–997.
- Holland, S. T., Tapp, M., Hildebrandt, D., Glasser, D. & Hausberger, B. (2004). Novel separation system design using “moving triangles”. *Computers and Chemical Engineering*, 29, 181–189.

- Hömmerich, U. & Rautenbach, R. (1998). Design and optimization of combined pervaporation/distillation processes for the production of MTBE. *Journal of Membrane Science*, 146, 53–64.
- Lu, Y., Zhang, L., Chen, H., Qian, Z. & Gao, C. (2002). Hybrid process of distillation side-connected with pervaporation for separation of Methanol/MTBE/C<sub>4</sub> mixture. *Desalination*, 149, 81–87.
- Peters, M., Kauchali, S., Hildebrandt, D. & Glasser, D. (Article submitted for publication). Membrane Residue Curve Maps: I. Derivation and Properties. *Submitted to Industrial and Engineering Chemistry Research*.
- Rehfinger, A. & Hoffmann, U. (1990). Kinetics of Methyl tertiary Butyl Ether liquid phase synthesis catalyzed by ion exchange resin – I. Intrinsic rate expression in liquid phase activities. *Chemical Engineering Science*, 45 (6), 1605–1617.
- Tapp, M., Holland, S. T., Hildebrandt, D. & Glasser, D. (2004). Column Profile Maps. 1. Derivation and Interpretation. *Industrial Engineering and Chemistry Research*, 43, 364–374.