

## HOW TO DECIDE WHEN AND HOW MUCH TO USE REACTIVE DISTILLATION

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Process design deals with synthesis and optimization tasks, where process synthesis means to conceive a set of processing units and the interconnections between these units which will fulfill the performance target of the process, and optimization means the evaluation of the best set of parameter values of the system. The intensive use of modular simulators, e.g. ASPEN PLUS<sup>®</sup> or numerical solver tools as gPROMS has hugely increased our ability of optimizing process structures; thus finding the set of alternatives solutions structures has become the key factor in the process design task.

Frey et al. [1] showed how knowledge of reactive distillations lines and potential reactive azeotropes can be used for the systematic design of reactive distillation processes. Hauan et al. [2] demonstrates how phenomena vectors may be used in the early stage of the design of reactive distillation columns for graphical determination of stationary points (reactive azeotropy) as possible boundaries of the feasible regions. They further showed how to use the length of phenomena vectors for preliminary design of complex hybrid process. However in this paper we use simple thermodynamics features given VLE data and preliminary kinetics considerations to show on practical ground the power of thermodynamics insights for the determination of the structure(s) in the early stage of process synthesis. Our interest in this paper is a quick and systematic geometric procedure for establishing whether reactive distillation is advantageous or not with regard to a particular system. The aim of the presented approach is to reduce the complexity of the combined process in order to enable simple structure solutions to be recognized quickly.

We consider a case study to illustrate the approach.

KEYWORDS: reactive distillation, process synthesis

### INTRODUCTION

Let us suppose that we have a process in which reaction and separation occur simultaneously. Let us suppose also that one has the possibility to switch on and off the reaction by introducing the catalyst. We consider the resultant process as a combination of the separation process and chemical reaction process. The global process occurring can be represented as:

$$\underline{p} = \alpha \underline{S} + \lambda \underline{r} \quad (1)$$

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where  $\underline{r}$  is the reaction vector,  $\underline{s}$  is the separation vector,  $\lambda$  and  $\alpha$  are scaling factors and  $\underline{p}$  is the combined process vector.

The normal classic optimization tries to optimize by choosing the parameter  $\lambda$  and  $\alpha$  but the difficulty is that  $\underline{s}$  and  $\underline{r}$  can bifurcate. In the present paper we introduce a simple graphical technique using thermodynamic features.

The framework of the approach consists of the following steps:

- Determination of the topology of the separation vector field.  
At infinite separation efficiency the trajectories of the distillation process for different initial compositions coincide with the residue curve map (RCM) which has been considered as a powerful tool for flowsheet (structures) development and feasibility analysis of conventional multi-component separation processes [3]. We first consider the location of the singular points of the system and then derive the possible distillation boundaries in the mass balance triangle (MBT). We then draw in the different separation regions defined by these boundaries the average directions of separation vectors. We will illustrate later this concept when dealing with a practical case.
- Determination of the chemical equilibrium line (surface).  
The chemical equilibrium curve represents the maximum degree of conversion of reagents for chemical systems and as such help to discern the forward reaction zone and to estimate when the chemical equilibrium conditions occur.
- Determination of optimum structure(s) for achievement of target objectives for the combined process.

### EXAMPLE: MTBE PROCESS SYNTHESIS

MTBE (Methyl tertiary butyl ether) was once seen as a replacement for lead additives in car fuel. It is produced from the reaction of methanol (MeOH) and isobutene (IBUT) with a catalyst in the liquid phase. This system has a complex separation sequence due to the high non-ideality of the system due to the polarity of the methanol compared with the non-polar MTBE product. The principal reaction is equilibrium limited and has the following stoichiometry:

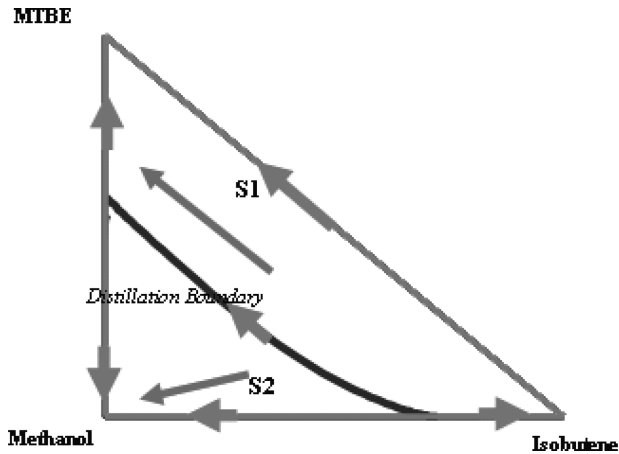


### THE TOPOLOGY OF THE SEPARATION VECTOR FIELD

The topology of the separation vector field is determined by the number and position of singular points. In this situation there are 3 pure components and 2 azeotropes. These 5 singular points divide the mole fraction composition space in 2 regions defining a distillation boundary inside the mass balance triangle (MBT).

Thus the essential topology of the separation vector field can be represented by the mass balance triangle and the boundary between the two regions as shown in Figure 1.

The total pressure  $P_{tot}$  of the system was set to 8 bars. The vapour pressure  $P_{vap}$  for each pure component has been calculated using the Antoine equation. The NRTL



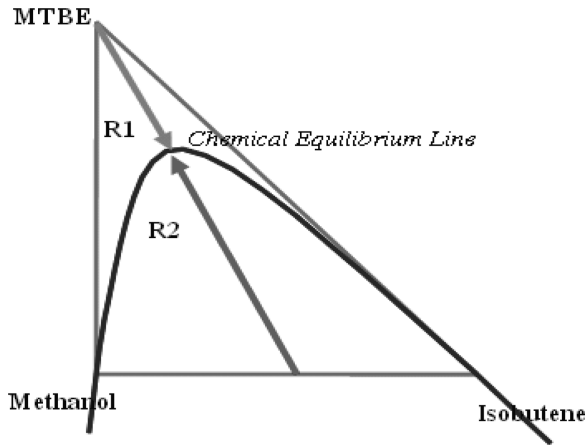
**Figure 1.** Distillation Regions for the MTBE system @ 8bar

(Non Random Two Liquid) model has been used to determine the liquid activity coefficient  $\gamma$ . The MTBE System binary parameters  $a_{ij}$ ,  $b_{ij}$ ,  $c_{ij}$  for the NRTL model are taken from the ASPEN PLUS<sup>®</sup> Databank.

All figures for the MTBE system are generated with these binary parameters at  $P_{tot} = 8$  bar.

**Table 1.** Thermodynamic data MTBE

Antoine equation	Methanol (1)	MTBE (2)	IBUT (3)
1	18.5875	3626.55	-34.29
2	15.883	2666.26	-53.7
3	15.7528	2125.75	-33.15
NRTL	$a_{ij}$	$a_{ji}$	$c_{ij} = c_{ji}$
1-2	-2.0302	0.049	0.3009
1-3	0.0	0.0	0.3067
2-3	6.5378	5.4988	0.3007
NRTL	$b_{ij}$	$b_{ji}$	$c_{ij} = c_{ji}$
1-2	448.6788	-21.974	0.3009
1-3	-234.1731	-157.658	0.3067
2-3	-2674.87	-2899.596	0.3007



**Figure 2.** Forward and Reverse chemical reaction zones for the MTBE system @ 8bar

From Figure 1, two separation regions may be schematically identified:

- Separation Region S1: Movement in this region is mainly such that the liquid composition becomes richer in MTBE as shown by the arrow
- Separation Region S2: Movement in this region will mainly be such that the methanol mole fraction in the liquid phase increases as shown by the arrow

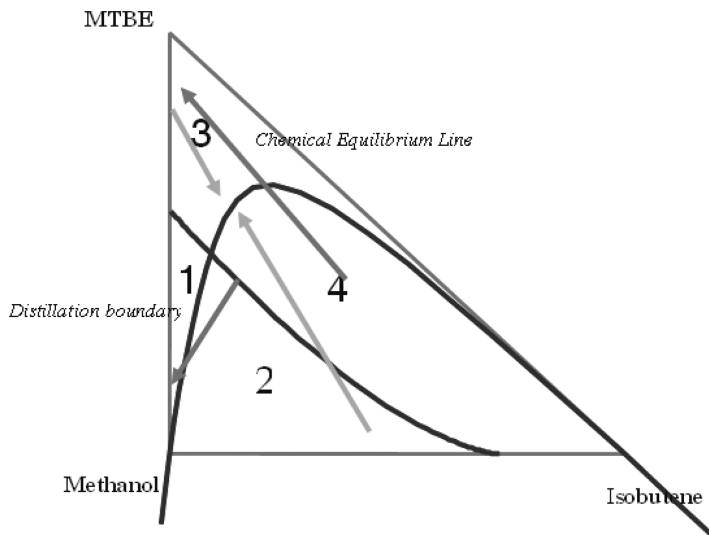
In each of the separation regions we represent the direction of the residue curves by average directions. The average direction represents the average change in the liquid composition during the boiling process.

#### THE CHEMICAL EQUILIBRIUM LINE (SURFACE)

The equilibrium constant is evaluated as a function of temperature from thermodynamics. Both the chemical equilibrium and rate equations with activities offer simple models with less parameters to fit. The kinetics are taken from Venimadhavan et al. [4]:

$$\ln(K_e) = \frac{6820}{T} - 16.33 \quad (3)$$

where  $K_e$  is the chemical equilibrium constant and  $T$  is the temperature in Kelvin. The chemical equilibrium that we consider describes both the thermodynamic (when the chemical affinity is null) and kinetic equilibrium compositions (when the rates of the forward and reverse reactions are equal). In Figure 2 we distinguish the reverse chemical zone (R1) and the forward chemical reaction zone (R2).



**Figure 3.** Properties of Regions of qualitatively different behaviour by superimposing the separation and reaction mass balance triangle for the MTBE system @ 8bar

### COMBINATION OF SEPARATION AND REACTION

In order to design a reactive distillation system we need to look at the way we combine the separation and reaction vector fields. Let us plot all the important features of the reaction and separation mass balance triangles on the same graph. We notice that we have four separate regions in Figure 3. In any of the four regions one will have qualitatively different behaviour.

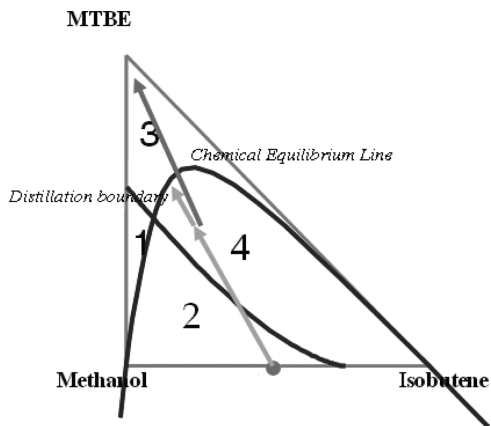
We suppose that the objective is that we would like to make as pure as possible MTBE in a process as simple as possible and we would also like to ensure we make significant quantities of the MTBE.

Let us look at each of the four regions separately and evaluate what is happening. Let us also suppose that one starts with an equimolar mixture of Methanol and Isobutene (stoichiometric ratio).

We evaluate the properties of the different regions in shown in Figure 3:

- Region 1 is such that reaction and separation are mainly toward component Methanol
- Region 2 is such that reaction is toward MTBE and separation to Methanol
- Region 3 is such that reaction and separation are mainly toward component MTBE
- Region 4 is such that reaction moves away from MTBE and separation to MTBE

We suppose that the initial material composition is an equimolar mixture of Methanol and Isobutene in region 2 as shown in Figure 4; one can see that the separation



**Figure 4.** Solution structure for the process synthesis of the MTBE system @ 8bar

will take us towards pure Methanol corner while reaction will take us to MTBE. So by using reaction only one can cross into region 4.

In region 4 both reaction and separation will move us towards region 3. Once we cross into region 3, reaction will take us back to reactants while separation will move us towards MTBE corner.

The strategy is to start with reaction alone (region 2) – in region 4 have simultaneous reaction and separation – in region 3 have separation alone as shown in Figure 4. By using this simple analysis we have obtained the sequences of the solution.

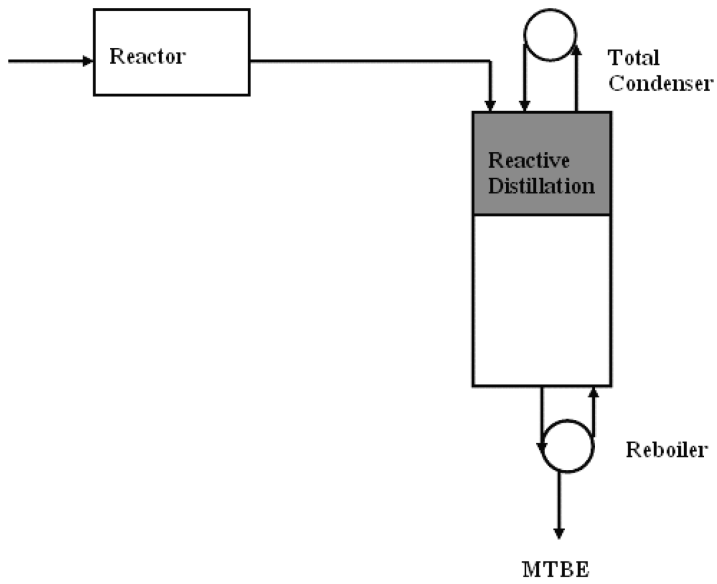
#### POSSIBLE PRACTICAL IMPLICATIONS

It is interesting to see what a reactive distillation column might look like that incorporates these ideas from above. A possible system that might incorporate these ideas is shown in Figure 5a.

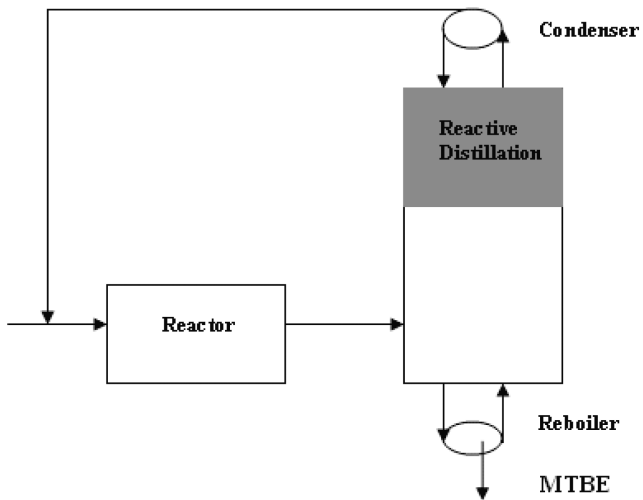
Interestingly this is not the same as the system usually used in industry as illustrated in Figure 5b. It would be of interest to do simulations and optimisations to see how the two systems compare each other.

#### DISCUSSION

This analysis has been done entirely using very simple thermodynamics data and so could be done at a very early stage of the analysis of a proposed process. The important result is that one is able to synthesise a structure for the system based only on this simple topological information. Once this has been done one is in a position to do a more detailed optimisation using more standard simulation techniques.



(a)



(b)

**Figure 5.** Possible equipments structure

Interestingly the proposed solution in this instance is one that in principle agrees with what one might expect if one used more sophisticated methods of analysis such as **Pontryagin's maximum principle**. In this case the process vector is an affine combination of two vectors. In this case one often finds that the solution has first the one process followed by a mixture of the two processes followed by the other process on its own [5]. Again in this case we would not find solutions which have parallel structures or recycles such as found in Figure 5b. It would be therefore of further interest to compare the results of Figures 5a and 5b.

## CONCLUSION

In this paper we produce simple diagrams based only on a minimum of thermodynamic information and using only topological information arrive at proposals for a structure that includes where to do separation and reaction either alone or together. Many current simulations can both simulate and optimise proposed structures. The part that is currently missing are methods to choose the structures. This paper suggests some initial ideas on how this might be done.

## ABBREVIATION

VLE	Vapour Liquid Equilibrium
MTBE	Methyl tertiary butyl ether
MeOH	Methanol
IBUT	Isobutene
MBT	Mass balance triangle
RCM	Residue curve map
$\underline{S}$	Separation vector
$\underline{r}$	Reaction vector
$\underline{p}$	Process vector
$K_e$	Chemical equilibrium constant
T	Temperature in Kelvin
$P_{tot}$	Total Pressure
$\alpha$	Scaling factor
$\lambda$	Scaling factor
$P_{vap}$	Vapour pressure

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