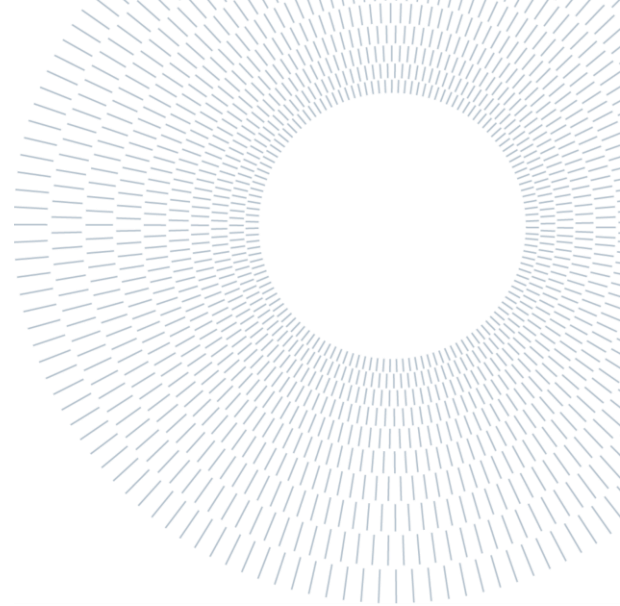




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EXECUTIVE SUMMARY OF THE THESIS

# Comparative techno-economic assessment between Reactive and Reactive-Cyclic distillation for Process Intensification: theoretical framework and application to MTBE and MeOAc Reactive Distillation

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

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**ACADEMIC YEAR: 2020-2021**

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## 1. Introduction

It is almost always true that the products of a chemical reaction are never only the desirable ones: the stream exiting from a reactor is always a mixture of desired product, unreacted reactants and by-products. That is why all the chemical plants always have a “reaction zone” and a “separation zone”, one to produce and one to split the products from the rest. The separation zone, in most cases, is the area that uses the biggest amount of energy: distillation is not only the most used process to separate the products, but also the most energy-consuming one. In recent years, global attention has shifted towards reducing environmental impact and energy consumption. To reduce both capital costs and energy consumption of the chemical industry, many studies started to deal with Process Intensification (PI): “any chemical engineering development that leads to a substantially smaller, cleaner and more efficient technology” [1]. Some of the most important technologies studied by PI comprehend

micro-reactors, membrane distillation, reactive separation, dividing-wall columns and periodic separation [2]. It is important to notice that, as the separation zone of a chemical plant is the one that requires the greatest amount of energy, small efficiency increases of the separating unit operations can lead to huge reduction of the energy consumption of the whole plant. In the last decades, reactive distillation and cyclic distillation have been widely studied and it has been demonstrated that individually they are good process intensifications; reactive distillation is capable of combining the reaction and the separation zones in the same unit operation, guaranteeing certain advantages to the resulting process: it is possible to reach higher conversions and selectivities removing continuously the formed product, breaking physical azeotropes and using the energy released by exothermic reactions to reduce the hot spots in the column and the heat that must be provided to the reboiler. Cyclic distillation should be able to prevent the mixing of the liquid phase on different trays, in this way the back-mixing is avoided and the efficiency of a

single stage can reach values also greater than 2 [3]. It gained new interest when Maleta [4] patented a new type of tray without downcomer that was able to ensure this feature. In theory, putting together the two PI, the resulting column should have the advantages brought by the two PI alone, that is why recently an interest on this hybrid version has started to grow, especially for those reactions (the slow ones) that cannot be performed in a conventional reactive column.

## 2. Methods

For the reactive columns the algorithm used to design the unit operation involves a reactive McCabe-Thiele method. A very important tool is the transformation of the system from a component based system to a reduced element based one: in this way a three component system can be reduced to a two element one simplifying a lot the computational effort. After that, it is possible to draw the chemical-physical equilibrium curves and draw in them the steps that represent the ideal stages that a RD column needs to carry out the reaction and the separation needed. In Figure 1 it is possible to see an example of this methodology.

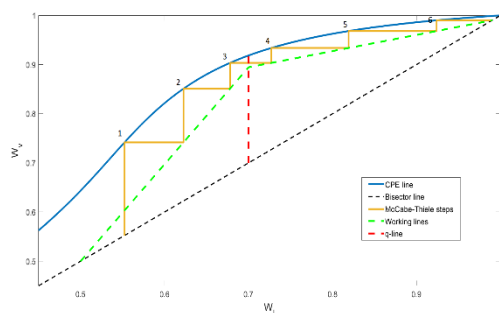


Figure 1: Example of McCabe-Thiele method

For the reactive-cyclic columns, as the technology is quite new, there are not many useful algorithms in the literature for modelling, sizing and simulating them. The few that exist, however, can be divided into two categories: chemical-physical equilibrium (CPE) based methods and rate based ones.

The first family of methods is very useful when the reaction involved is fast and it reaches the chemical equilibrium in a very short amount of time. The algorithm studied was perfected by Nielsen [5] and it requires the simultaneous resolution of the chemical and the physical equilibrium equations in

the element domain. The algorithms needs that the bottom compositions and external flowrates must be fixed along with the element vapour flow rate per cycle and the reboiler hold up, then it is possible to run a backward integration going up in the column until the composition on the trays meets the composition of the feed; after assigning the feed tray, the backward integration restarts to reach the top design composition of the distillate. The second family of methods can be used also for reactions that do not reach equilibrium; this kind of algorithms are based on the expression of a kinetic law capable of describing the reaction involved in the process in exam. The algorithm used to design the columns has been proposed by Pătruț et al. [6] and it resembles the one used for pure cyclic distillation towers. It is based on a backward-integration just like the CPE method presented before, but this time this feature is applied only on the stripping zone: the column is indeed divided in three distinct zones, rectifying-reactive-stripping, and the three are designed in three different ways; the stripping zone is designed with the backward-integration after that the conversion, the purities of the products, the feed flow and composition, the external vapour flow and the duration of the vapour flow period are specified; the backward-integration stops when it is reached a zone where there is no more change in tray composition between two adjacent trays. After that, this last tray of the stripping section is taken as a reference to evaluate a predicted mean reaction rate that is then used in the following formula to evaluate the number of reactive trays:

$$N_{cat} = \frac{m_{cat}}{m_{tray,cat}} = \frac{F * \xi}{r_{av} * m_{tray,cat}}$$

Lastly, the rectifying zone is designed by trial and error on the number of reactive trays needed to fulfil the required specifics.

This approach is very helpful because it is capable of reducing a lot the computational effort due to the design of the reactive zone. The major drawback lies in the fact that the formula reported above overestimates the number of reactive trays because it is based on a mean reaction rate that in reality is not always the same throughout the whole reactive zone of the column.

After the design, each reactive column has been simulated on Aspen Hysys and each reactive-cyclic column has been simulated thanks to a rigorous model on MATLAB until pseudo-steady state.

### 3. Case studies

The methods presented above have been applied to two different case studies:

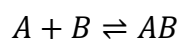
- MTBE production from isobutene and methanol, as an example of fast reaction;
- MeOAc production from acetic acid and methanol, as an example of slow reaction.

The two cases have been chosen among the other examples because these are two of the most studied.

The reactive columns and the reactive-cyclic columns of the two cases have been designed with the algorithm presented above, then simulated and dimensioned to avoid weeping and flooding (for the Maleta trays there is actually no correlation for flooding so, for the reactive-cyclic columns, just the weeping condition was investigated). After that, the cost of each configuration was estimated in terms of CAPEX (with Guthrie's formula applied to the columns, the trays and the two exchangers) and in terms of OPEX (evaluating how much cooling water and steam were necessary for each column to work properly).

#### 3.1. Fast reaction: MTBE

The system has been studied for both cases in the element domain.



where A stands for the isobutene and B stands for the methanol.

The design specifications valid for both the columns can be summed up in the following table:

P [atm]	$W_A^F$	$W_A^D$	$W_A^B$	Catalyst	Cat. amount [mol/L]
3	0,7	0,99	0,5	$H_2SO_4$	1

For the reactive-cyclic column, a vapour flow period of 10 seconds has been chosen.

The results of the design and simulations performed on the reactive column show that it is necessary to work with 13 rectifying stages, 3 reactive trays and 15 stripping stages (including the reboiler).

The reactive cyclic column instead is capable of reaching the same productivity just with 1 rectifying stage, 3 reactive trays and 3 stripping

stages (including the reboiler) hence reducing drastically the height of the column and so also the capital expenditures. The major concern regarding this configuration rely in the fact that to guarantee the same productivity and the same specifics, it is necessary to enhance the energy consumption of the unit operation. In the following table it is possible to see the different amounts of energy required for the two processes.

	$Q_c$ [kW]	$Q_r$ [kW]
<b>Reactive</b>	165,6	71
<b>Reactive-cyclic</b>	303,8	155,1

#### 3.2. Slow reaction: MeOAc

The design specifications valid for the reactive column can be summed up in the following table:

P [atm]	$z_F$	$x_{MeOAc}^D$	$\xi$	Catalyst	Cat. amount [kg]
1	0,5	0,95	> 90%	NKC-9	25

The results of the design and simulations performed on the reactive column show that it is necessary to work with 2 rectifying stages, 33 reactive trays and 3 stripping stages (including the reboiler).

The design specifications valid for the reactive-cyclic column can be summed up in the following table:

P [atm]	$z_F$	$x_{MeOAc}^D$	$x_{AcOH}^D$	Catalyst	Cat. amount [kg]
1	0,5	> 0,95	< 0,005	NKC-9	25

The results of the design and simulations performed on the reactive-cyclic column show that it is necessary to work with 5 rectifying stages, 17 reactive trays and 4 stripping stages (including the reboiler).

It is quite clear that also in this case, there is a reduction of the number of trays and so the column with the cyclic feature results to be smaller and more compact, but just like the fast case, the major

concern regarding this configuration rely in the fact that to guarantee the same productivity and the same specifics, it is necessary to enhance the energy consumption of the unit operation. In the following table it is possible to see the different amounts of energy required for the two processes.

	$Q_c$ [kW]	$Q_r$ [kW]
<b>Reactive</b>	262,5	146,7
<b>Reactive-cyclic (tliq = 10 s)</b>	347,4	328,2
<b>Reactive-cyclic (tliq = 30 s)</b>	304,4	287,6

The table above shows two different reactive-cyclic columns: they both have the same vapour flow period time (120 seconds) but differ one from the other for the duration of the liquid flow period. It is important to stress out the fact that the reaction does not happen just during the VFP, but also during the LFP even though there is less mixing on the trays (i.e. there are no vapour bubbles climbing the tower).

## 4. Conclusions

This thesis work has been conducted to investigate whether the cyclic feature can be a valid option to make the reactive columns work better. The study conducted on the MTBE case shows that including the cyclic feature when dealing with a very fast reaction could be a viable option to reduce drastically the number of stages and so the dimensions of the column: the reactive column needs 30 trays while the reactive cyclic can do the same job using only 6 trays. The direct consequence of this result is the fact that also the capital expenditures are reduced in the same way, especially the ones of the column alone. What makes the reactive columns still a better solution to implement is the fact that more energy should be consumed to make the reactive-cyclic columns work and, in the long term, also more money because just after one year and a half, the total costs of the reactive-cyclic column become higher than the total costs of the pure reactive tower.

The same kind of conclusions can be taken also for the case of the Methyl Acetate synthesis. The cyclic feature is a good way to reduce the number of trays and so the total height of the columns, but in this case the capital expenditures do not decrease because the diameter of the columns gets bigger so

the CAPEX remains quite similar between the reactive and the reactive-cyclic cases. Also for the slow reactions, it seems that the cyclic feature does not give proper improvements to the process; even though the purity remains the same and the productivity can be modulated to be the same of a reactive tower, the columns without the cyclic feature seem to be less energy consuming and also cheaper.

It seems that the cyclic feature does not give the expected results when added to a reactive column, but it is important to stress out that new studies should be done to investigate further what would happen with different types of reactions. It could be interesting to make a more general study about what is and what is not a fast reaction suitable for reactive distillation and to apply then the cyclic feature on a general model of slow reaction to see when and how the addition of this feature could bring improvement in the process.

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**POLITECNICO DI MILANO**

School of Industrial and Information Engineering

Master of Science in Chemical Engineering

Department of Chemistry, Material and Chemical Engineering "Giulio Natta"



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Comparative techno-economic assessment between Reactive  
and Reactive-Cyclic distillation for Process Intensification:  
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in collaboration with

Process and Systems Engineering Center (PROSYS), Department of Chemical and Biochemical  
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***Academic Year: 2020/2021***

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# Abstract

Cyclic distillation has gained in the recent years more and more interest, both for academic and industrial scopes. The reason lies in the fact that the periodic operation applied to the distillation is able to increase the efficiencies of the single trays avoiding the phenomenon of the backmixing on the trays.

Recently, this feature has been applied also to reactive distillation to understand whether it could be a viable option to combine the two different process intensification to collect the advantages of both.

In this work, the two combined feature will be analysed to understand if adding the cyclic option to a reactive column could be a good intensification of the process in terms of purity of the products, energy savings and costs.

The study has been conducted on two different case studies that refer to two distinct types of reactions: MTBE synthesis has been chosen to be an example of fast reaction while MeOAc synthesis has been chosen to be an example of slow reaction; both of the two have been adopted because there are lots of examples of their applications in reactive towers.

After designing the columns with one of the available algorithms present in literature, each column has been then simulated with a rigorous model, dimensioned and then analysed in terms of cost of the column, of the exchangers and of the utilities.

Finally, all these information have been used to compare the reactive towers with and without the cyclic feature.



## Sommario

La distillazione ciclica ha riscosso negli ultimi anni sempre più interesse, sia in ambito accademico che industriale. Il motivo risiede nel fatto che la periodicità, applicata alla distillazione, è in grado di aumentare le efficienze dei singoli piatti evitando il fenomeno del rimescolamento.

Recentemente questa caratteristica è stata applicata anche alla distillazione reattiva per studiare se potrebbe essere una valida opzione combinare le due diverse intensificazioni di processo per raccogliere i vantaggi di entrambe.

In questo lavoro verranno analizzate le due caratteristiche combinate per capire se rendere ciclica una colonna reattiva risulterebbe in una buona intensificazione del processo in termini di purezza dei prodotti, risparmio energetico e costi.

Lo studio è stato condotto su due diversi casi studio che si riferiscono a due distinti tipi di reazioni: la sintesi del MTBE è stata scelta come esempio di reazione veloce mentre la sintesi del MeOAc è stata scelta come esempio di reazione lenta; entrambi sono stati adottati perché sono presenti già molti esempi di loro applicazioni in torri reattive.

Dopo aver progettato le colonne con uno degli algoritmi disponibili in letteratura, ogni colonna è stata poi simulata con un modello rigoroso, dimensionata e poi analizzata in termini di costo della colonna, degli scambiatori e delle utenze.

Infine, tutte queste informazioni sono state utilizzate per fare un confronto tra le torri reattive standard e le torri reattive e cicliche.

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# 1. Introduction

It is almost always true that the products of a chemical reaction are never only the desirable ones: the stream exiting from a reactor is always a mixture of desired product, unreacted reactants and by-products.

To meet the specifics required by the subsequent users (client, downstream processes, etc.), the outlet mixture has to be separated in different streams with certain compositions that can be recycled back in the plant (unreacted reactant), used to produce energy or collected to be wasted (by-products), sold or used in the following steps of the process (desired products). The majority of the chemical plants can always be divided in “reaction zone” and “separation zone”: the first comprehends only the reactor(s); while the second includes all the unit operations following it (them); an example is reported in Figure 1 that shows the conceptual design of an Ibuprofen production plant. The separation zone, in most cases, is the area that uses the biggest amount of energy: distillation is not only the most used process to separate the products, but also the most energy-consuming one; it accounts for 5-10% of the world’s energy consumption.

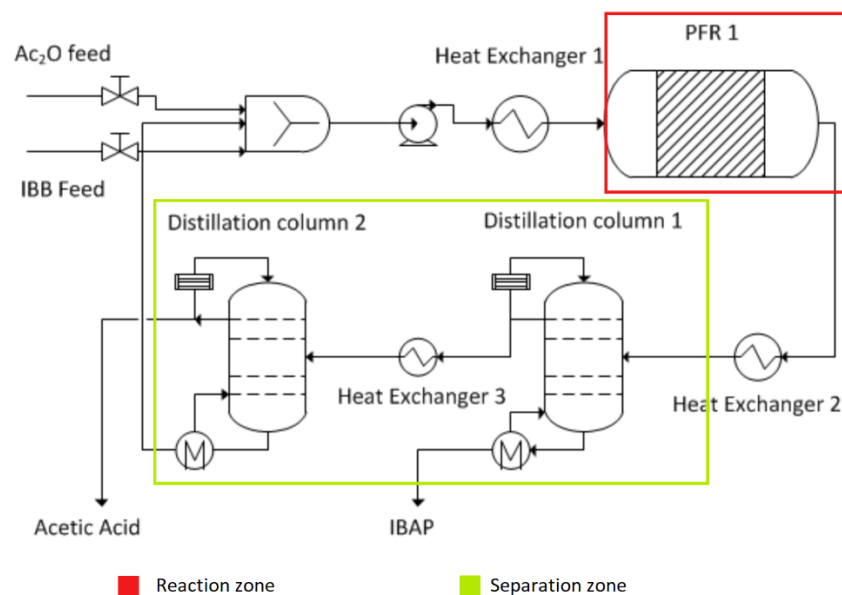


Figure 1: Reaction and separation zone in an Ibuprofen production plant.

In recent years, global attention has shifted towards reducing environmental impact and energy consumption. First in 2008 and then in 2014, EU adopted two energy and climate packages containing the environmental goals for the 2020 and 2030 [1, 2]. To reduce both capital costs and energy consumption of the chemical industry, many studies started to deal with Process Intensification (PI): “any chemical engineering development that leads to a substantially smaller, cleaner and more efficient technology” [3]. Indeed, the International Energy Agency recognizes energy efficiency as the world’s “first fuel”, worth between USD 310 billion and USD 360 billion in 2012 [1]. Some of the most important technologies studied by PI comprehend micro-reactors, membrane distillation, reactive separation, dividing-wall columns and periodic separation [4]. It is important to notice that, as the separation zone of a chemical plant is the one that requires the greatest amount of energy, small efficiency increases of the separating unit operations can lead to huge reduction of the energy consumption of the whole plant.

In the next sections, it is possible to find a brief introduction of what is Process Intensification and the concepts and principles of reactive separation and cyclic distillation technologies.

## 1.1 Process intensification

The major innovations of the chemical industry have been brought by a field of study called Process Intensification (PI). Its aim is the design and modelling of new kind of technologies that differ from the old ones because they are usually smaller, cleaner and more energy efficient.

“Process Intensification” was used for the first time in 1973 by Leszczynski, but there is still no clear definition of PI that all agree on [5]:

- In 1983 Ramshaw and Arkley [6] stated that PI is the devising exceedingly compact plant which reduces both the ‘main plant item’ and the installations costs, providing then a definition that was based merely on the number of devices and on the cost of the plant.
- Cross and Ramshaw in 1986 [7] added that PI is the strategy of reducing the size of chemical plant needed to achieve a given production objective.

- The two definitions above were “mixed” in 2003 by Tsouris and Porcelli [8] : PI refers to technologies that replace large, expensive, energy-intensive equipment or process with ones that are smaller, less costly, more efficient or that combine multiple operations into fewer devices (or a single apparatus).
- The first that included the concept of global optimization were Portha et al. [9] that in 2014 stated that PI is a holistic overall process based intensification (i.e. global process intensification) in contrast to the classical approach of process intensification based on the use of techniques and methods for the drastic improvement of the efficiency of a single unit or device.
- Finally Baldea [10] in 2015 proposed a definition based also on the safety: PI is any chemical engineering development that leads to substantially smaller, cleaner, safer and more energy efficient technology or that combine[s] multiple operations into fewer devices (or a single apparatus).

The guiding principle for PI were summarized by Van Gerven and Stankiewicz [11] :

- Maximize the effectiveness of intramolecular and intermolecular events: catalysis is the core aspect linked to this first principle.
- Provide all molecules the same process experience: it could be reached by the use of static mixers which offer a very intensive mixing and so enhances the specific interfacial areas for mass transfer.
- Optimize driving forces at all scales and maximize the specific surface areas to which they apply: this principle can be achieved improving transport of mass and heat using for example micro-reactors and pore structures.
- Maximize synergistic effects from partial processes: the use of combined devices such as reactive distillation can guarantee a major synergy between the reaction and the separation phase (i.e. breaking of azeotropes, elimination of side reaction).

It is clear from the various definitions and from the guiding principle that PI takes some quite challenging tasks. It is of paramount importance to design processes that are capable of reaching the same (or also better) specifics for the final products but using less energy, less space, less

equipment. The grade of complexity of a PI design project is far higher than the design of a “standard” version of the same equipment.

The real challenge lies in the fact that to build these new kinds of technologies it is important not only to change the technologies, but also to change the way of designing them. Portha et al [9] for example proposed a different view: they distinguished between local intensification and global intensification addressing that the classical methods were all based on the local intensification of the single units; the result of the local intensifications discards all the strong interactions between units and the obvious consequence is a weak improvement for the whole process. Global intensification leads to a process that is fully optimized even if the single units do not work at their optimal point but is clearly more difficult and time consuming (also from a computational point of view). Portha et al stated that a two-step approach should be more advantageous: first, a global intensification of the whole performance of the global process; second, local intensification by classical techniques.

There are quite a lot of unit operations that are the offspring of the Process Intensification. It follows a brief summary of three of the most studied (reactive distillation and cyclic distillation will be treated in the following two paragraphs):

- Microfluidic technology: Ramshaw [6] pioneered this technology having as objective reducing costs, low energy consumption, high safety, less waste, etc. Microreactors allow to work with high pressures and temperatures because thanks to the small sizes and so the increased efficiencies it is possible to use very low amount of energy to enhance the temperature and so to reduce the residence times of the reactions involved. The main disadvantage is the intrinsic impossibility to replace the catalyst; it is necessary to use then catalyst that are regenerable in situ.
- Internally heat integrated distillation columns: the first that suggested to modify the energy paths of a distillation columns was Freshwater [12] in 1951; he thought that transferring energy from the reboiler to the condenser would have reduced the temperature lift by a heat pump. The technology was furtherly studied and perfected: heat can be transferred from a hotter rectification section (operated at higher pressure)

to the colder stripping section, giving the process high energy efficiency and the possibility to work (in the ideal case) without condenser and reboiler [13].

- Dividing wall column: DWC is an implementation of a thermally coupled distillation design already investigated in the years. The vertical walls avoid radial mixing of vapour and liquid streams and enable the withdrawal of three products with any thermodynamically feasible purity in one single column. It is very useful to include two conventional distillation columns in series (to separate three component mixtures) into a single shell.

## 1.2 Reactive distillation

The goal of reactive separation, shown in Figure 2, is to combine the reaction and the separation steps of a process.

The reactants are sent to a column where both the reaction and the separation of the products occur in the same place. The products are collected in the distillate or in the bottom of the column according to the different volatilities of the compounds. The trays in the column can be either filled with catalyst (heterogeneous catalysis), or empty (homogeneous catalysis) but in this latter case, after the reactive separation there is the need of another column to separate the catalyst from the products.

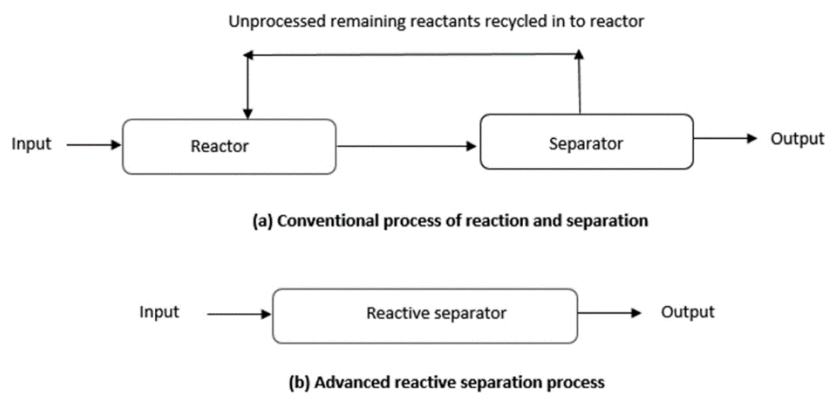


Figure 2: a) Conventional process - b) Reactive distillation



Reactive separation has shown its advantages since 1921 when Backhaus [14] took the first patent for a reactive column for the production of esters. It is important to remember that one of the best examples of the benefits of the reactive distillation is shown by the production of Methyl Acetate started in 1983 by Eastman Chemical [15]. The standard process, in Figure 3a, requires at least eight standard columns, one extractive column, one decanter and one reactor: the product mixture can form azeotropes and, in the reaction involved, the equilibrium is shifted to the reactants so a lot of columns and big recycles are needed to guarantee a good conversion and separation. A simple reactive column, shown in Figure 3b can replace everything: the process scheme is far simpler and the costs are strongly reduced.

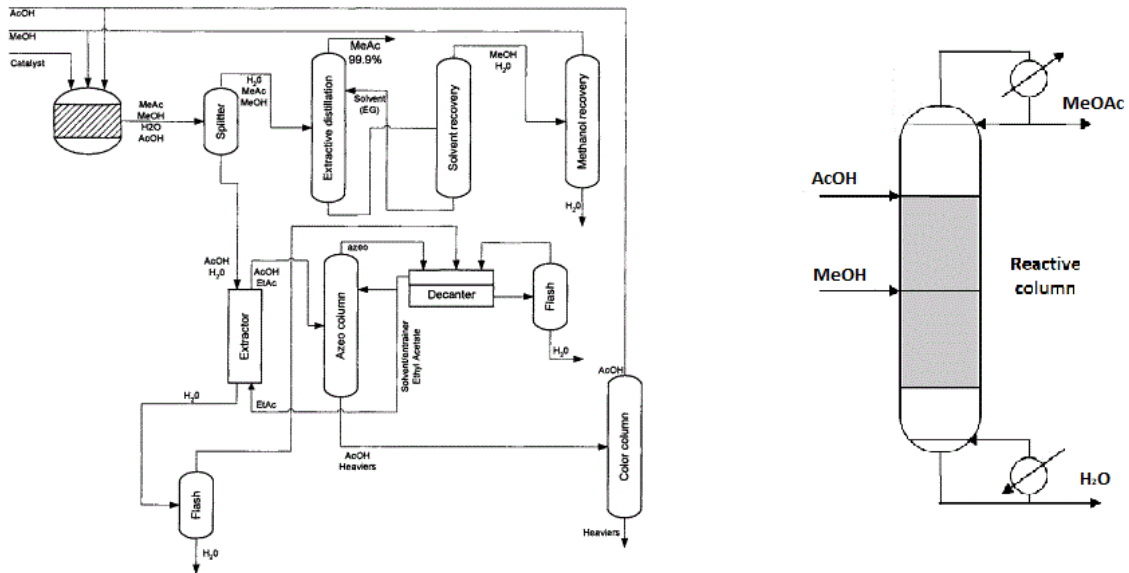


Figure 3: a) MeOAc standard production plant PFD - b) MeOAc production with reactive distillation

The main advantages and disadvantages of reactive separation are listed below:

- ✓ It is possible to reach a higher conversion and to remove recycles from the process scheme: the continuous removal of the products within the reactive volume pushes the equilibrium towards the products (Le Chatelier principle) so it is possible to consume almost all the reactants (high conversion) and to avoid the necessity of recycles;

- ✓ It is possible to have higher selectivity when there are reactions in series, thanks to the continuous removal of products [15];
- ✓ Physical azeotropes can be avoided [15];
- ✓ If the reaction is exothermic, the heat of reaction can be used to vaporize partially the mixture on the stages and so to reduce the utility consumption at the reboiler [15];
- ✓ The energy released by the (exothermic) reaction will be used to vaporize the separating liquid mixture; therefore, the column is more controllable because of the absence of hot spots [15];
- ✓ It is possible to make the process scheme more easily readable and cheaper;
- ✗ To enhance more the process, it is important that all the components (both reactants and products) have the “correct” volatility: only if the reactants and the by-products are middle-boiling compounds and the products are either high or low-boiling compounds, the desired ones will be continuously removed from the top or the bottom and so the equilibria of the reactions involved will be furtherly pushed towards their formation [16];
- ✗ Operating temperature and pressure must be compatible both with the separation and with the reaction [16];
- ✗ The reaction needs to be fast in comparison to the liquid residence time on the stage [16];
- ✗ Reactive azeotropes could limit column performance.

### 1.3 Cyclic distillation

Cyclic distillation (or Periodic Separation) firstly appeared in the 1950s when a group headed by Cannon [17] started to study the possibility of transforming standard operations (e.g. liquid-liquid extraction, particle separation, adsorption and distillation) into periodic ones.

Periodic Separation is different from standard distillation because the vapour and the liquid phases do not flow together in the column: Figure 4 shows that one cycle of operation is divided in two periods, the Vapour Flow Period (VFP) and the Liquid Flow Period (LFP). During VFP the valves that control reflux and feed entrances in the column are closed and the vapour coming from the reboiler is free to rise in the column and exchange mass and energy with the liquid

standing on each tray; the vapour flows in the column for a certain time  $t_p$ , a design parameter that has to be chosen to guarantee a certain ratio between the vapour rising and the liquid hold up [18]. After the VFP, the vapour is stopped and the LFP starts; in this period, the liquid from an upper tray is discharged onto the stage immediately below, the reflux is sent back in the column and the feed enters on the feed tray.

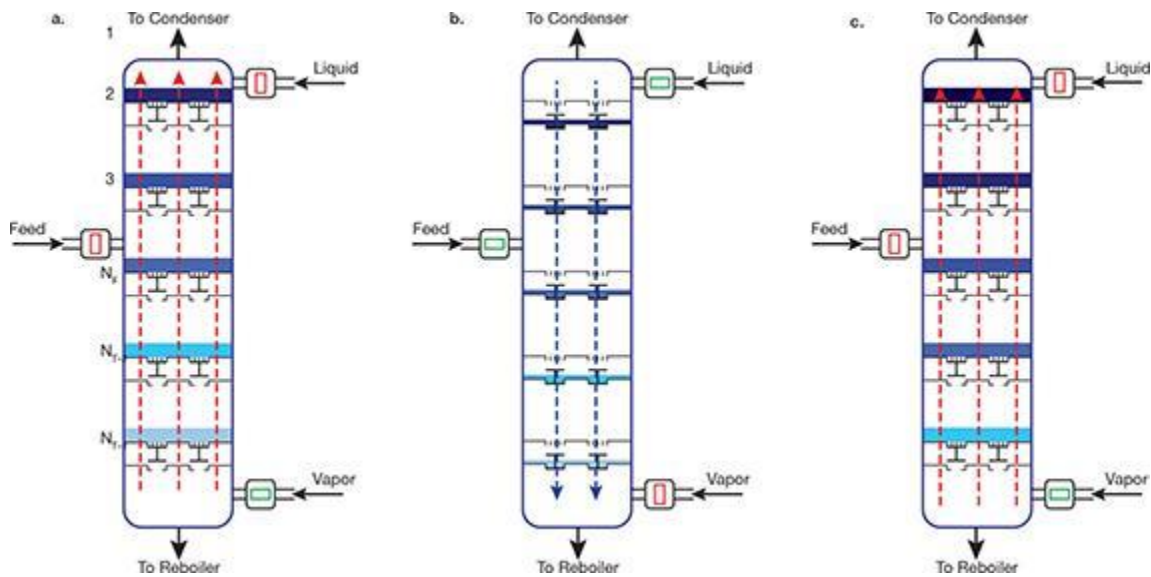


Figure 4: Cyclic distillation: a) VFP - b) LFP - c) Start of the following cycle.

Ideally, a cyclic column should be able to prevent the mixing of the liquid phase on different trays, in this way the back-mixing is avoided and the efficiency of a single stage can reach values also greater than 2 [19].

Theoretically speaking, the cyclic column is simple to implement in a real plant because the only modification that has to be done is the replacement of the standard trays with the cyclic ones. With the conventional trays (sieve, screen, packed) without downcomer, it was difficult to avoid the back-mixing of the liquid on the different stages [17, 20, 21], but in 2011 Maleta [22] patented a new type of tray that could prevent this problem.

The key factors of Maleta trays are the presence of vapour-moved pistons, which seal the liquid holes during the VFP, and the sluice chambers, a zone of transition between LFP and the following VFP. Figure 5 clearly shows that at the beginning of the LFP the liquid on a tray is collected first in the sluice chamber and then, when the VFP starts, on the tray below.

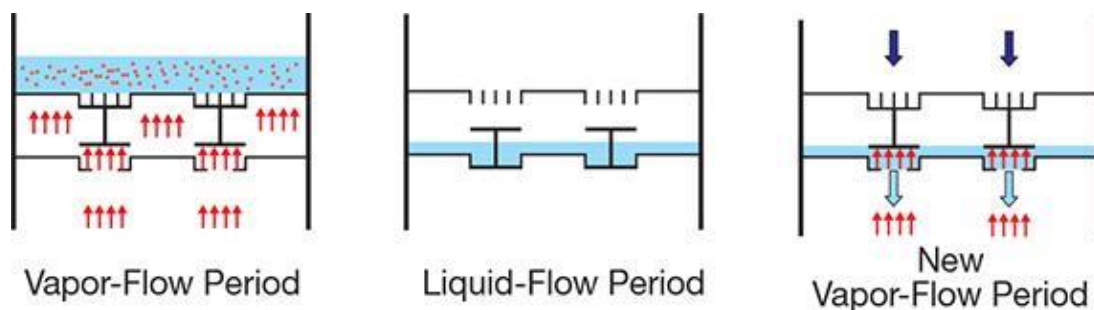


Figure 5: Maleta [22] trays

Recently, Toftegård et al. [23] presented a new kind of cyclic tray in which the pistons are controlled pneumatically and not moved by the vapour. The advantage of this new technology lies in the fact that it is possible to make the vapour rise in the column continuously in order to avoid high-pressure build up in the reboiler.

#### 1.4 Reactive-Cyclic distillation

In the recent years, a growing interest has been shown towards a possible hybrid of the two technologies presented above. At the current time, just a few papers are present in literature, but this new technology could be another possible improvement in the PFDs of the future. From a practical point of view, it should be quite simple to implement it because the only change added to a cyclic column would be the one of introducing a catalyst on some trays to make a reaction happen.

In theory, this technology should be able to group all the benefits taken from the reactive and the cyclic intensification alone and it should be also applicable on a certain range of reactions

that could not be carried out in the reactive columns: some slower reactions could be conducted in the reactive-cyclic columns because the residence time on each tray can be better controlled with the cyclic feature.

It is not simple to design and simulate a column of this type because of its increased complexity, that is the main reason because there are still no columns of this type operating in the world. It is important to notice that even if the actual design methods are still not perfect, it is already possible to design and simulate this type of system to understand if it will be or not a good feature to implement in the future chemical plants.

## 1.5 Problem Statement

The aim of this project is to verify whether the periodic reactive distillation is a viable option both for the fast reactions and for the slow ones. To do so, two key cases will be studied: the MTBE production from isobutene and methanol, as an example of fast reaction, and the production of methyl acetate from acetic acid and methanol, as an example of slow reaction. These two cases have been chosen because the reactive distillation is already a good intensification of their traditional method of synthesis and the reactive case of both has been already studied widely.

Both the cases will be treated in the same way: the columns will be firstly designed with one of the few design methods available in literature, then a rigorous simulation will be done to have more accurate data and lastly for each technology there will be a cost analysis based on the evaluation of the total annualized costs of the equipment and the utilities. To understand if the reactive-cyclic technology can be a better option, the results of the cost analysis will be compared with the results of the cost analysis of reactive towers that can reach the same productivity of the desired product.

For the MTBE case, some of the reactive columns will be designed by employing the driving force-based method because this procedure has shown in some studies [24, 25] that its application is useful both to reduce the energy consumption for the reboiler and the condenser of the column and to guarantee a better controllability.

## 2. Theoretical basis

In this chapter, the theoretical basis used in this work to design and simulate the reactive and reactive-cyclic columns will be presented. The concepts of physical and chemical equilibrium, element representation and chemical-physical equilibrium (CPE) will be briefly exploited.

### 2.1 Physical Equilibrium

For a simple distillation column, the physical equilibrium is the only one considered; the physical equilibrium is the equilibrium between different phases.

When dealing with a mixture, the partial pressure of each component can be modelled simply by the Raoult's law [26]:

$$P_i = Py_i = P_i^{sat} x_i$$

In the equation above,  $P_i^{sat}$  is the vapour pressure of the component  $i$ ,  $y_i$  is the molar fraction of the component  $i$  in the vapour phase and  $x_i$  is the molar fraction of the component  $i$  in the liquid phase.

This kind of equation can be used as a good approximation when the liquid mixture can be compared to an ideal mixture; to be more accurate and to describe the behaviour of a wider range of mixtures, it is possible to use the modified version of the Raoult's law:

$$P_i = Py_i = P_i^{sat} x_i \gamma_i$$

where  $\gamma_i$  is the activity coefficient of the component  $i$ ; the coefficient  $\gamma_i$  of each component can be calculated with the proper activity coefficient model (i.e., Wilson, NRTL, UNIQUAC, UNIFAC).

The last term that must be investigated to evaluate the physical equilibrium is the vapour pressure; it is usually [26] evaluated thanks to an equation in the form (Antoine's equation):

$$\log(P_i^{sat}) = A - \frac{B}{T + C}$$

## 2.2 Chemical Equilibrium

The chemical equilibrium for a closed system is the state in which the reaction rates of the direct and the inverse reactions are equal, therefore the composition of the mixture remains constant. In a conventional distillation column, each tray can be considered at equilibrium only when the whole column is at steady state: the tray is not a closed system because of the liquid and gaseous streams reaching and leaving it all the time, but these flows become constant when steady state is reached and so also the composition and the reaction rate on each tray becomes constant.

The chemical equilibrium is directly linked to the Gibbs free energy of reaction [27]:

$$\Delta G_r = \Delta G_r^0 + RT \ln(K)$$

The equilibrium is reached when  $\Delta G_r$  is equal to 0, so rearranging the previous equation:

$$K_{eq} = \exp\left(-\frac{\Delta G_r^0}{RT}\right)$$

$\Delta G_r^0$  can be evaluated experimentally or with the Van't-Hoff equation that expresses the Gibbs free energy of reaction in function of the temperature of the system.

The equilibrium constant is also related to the compositions of the components in the system by the equation:

$$K_{eq} = \prod_{i=1}^{NC} (x_i \gamma_i)^{\nu_i}$$

Imposing the equality between the two equations above, it is then possible to evaluate the composition of the system at equilibrium.

## 2.3 Element based representation

It is useful to express the composition of multicomponent systems in terms of a reduced number of elements. This transformation is useful to give a simpler way to evaluate and to visualize the composition of the systems with more than 2 components.



To identify the elements, it is important to start from the Gibbs' phase rule for the reactive systems. Table 1 gives a panoramic of the number of intensive variables and constraints in a reactive system.

Table 1: Intensive variables and constraints in a reactive system

<i>Intensive variables</i>	
<i>Temperature in each phase</i>	$NP$
<i>Pressure in each phase</i>	$NP$
<i>Composition in each phase</i>	$NP(NC - 1)$
<i>Total variables</i>	$NP(NC + 1)$
<i>Constraints</i>	
<i>Equality of <math>T</math></i>	$NP - 1$
<i>Equality of <math>P</math></i>	$NP - 1$
<i>Equality of <math>\mu</math> for each component</i>	$NC(NP - 1)$
<i>Equality of <math>K</math> for each reaction</i>	$NR$
<i>Total constraints</i>	$2NP - 2 + NC * NP - NC - NR$

The degrees of freedom for the system can be calculated as

$$F = Var - Con = 2 - NP + NC - NR$$

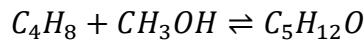
In the presence of a non-reactive system, the term  $NR$  would be equal to zero, so it is clear that a reactive system presents  $NR$  degrees of freedom less than a non-reactive one if the number of components and the number of phases are equal. The number of elements of a system with the same degrees of freedom can be compared to the number of components of a system when the number of reactions is equal to zero:

$$NC - NR = NE - 0 \quad \Rightarrow \quad NE = NC - NR$$

So, the phase rule for a reactive system can be expressed as

$$F = 2 - NP + NE$$

To identify the elements, it is also possible to start from the atom-species matrix, find the rank of the matrix and reduce the matrix in the diagonal form. The following example is taken from Pérez-Cisneros [28] and it deals with the identification of the elements in the MTBE reactive system:



$$\mathbf{A}_e = \begin{matrix} C \\ H \\ O \end{matrix} \begin{bmatrix} 4 & 1 & 5 \\ 8 & 4 & 12 \\ 0 & 1 & 1 \end{bmatrix}$$

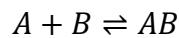
Performing row operations, it is possible to reach the reduced diagonal form of the matrix  $\mathbf{A}$  that is equal to

$$\mathbf{A} = \begin{matrix} A \\ B \end{matrix} \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix}$$

The rank of the matrix is equal to 2 and it is consistent with the rule found before:

$$NE = \text{rank}(\mathbf{A}_e) = NC - NR = 3 - 1 = 2$$

The reaction equation can be then expressed also in the element domain:



where the element A corresponds to the isobutene, the element B corresponds to the methanol and AB is how MTBE is called in the element domain; the reduced matrix  $\mathbf{A}$  is important because it is a powerful tool to transform all the useful quantities from the components domain to the element one.

The amount of moles of element  $j$  can be expressed [28] as:

$$b_j = \sum_{i=1}^{NC} A_{ji} n_i$$

The total amount of element moles can be expressed as

$$b_T = \sum_{j=1}^{NE} b_j = \sum_{j=1}^{NE} \sum_{i=1}^{NC} A_{ji} n_i$$

Liquid and vapour mole fractions of elements can be calculated as

$$W_j^l = \frac{b_j^l}{b_T^l} \quad \text{and} \quad W_j^v = \frac{b_j^v}{b_T^v}$$

These two can be also expressed in terms of component mole fractions. For the liquid one (the vapour case is identical):

$$W_j^l = \frac{b_j^l}{b_T^l} = \frac{\sum_{i=1}^{NC} A_{ji} n_i^l}{\sum_{k=1}^{NE} \sum_{i=1}^{NC} A_{ki} n_i^l}$$

The liquid component mole fraction is given by:

$$x_i = \frac{n_i^l}{\sum n_i^l} \quad \Rightarrow \quad n_i^l = x_i \sum n_i^l$$

And so:

$$W_j^l = \frac{b_j^l}{b_T^l} = \frac{\sum_{i=1}^{NC} A_{ji} x_i \sum n_i^l}{\sum_{k=1}^{NE} \sum_{i=1}^{NC} A_{ki} x_i \sum n_i^l} = \frac{\sum_{i=1}^{NC} A_{ji} x_i}{\sum_{k=1}^{NE} \sum_{i=1}^{NC} A_{ki} x_i}$$

The equation is valid also for the vapour phase changing the quotes in v.

An example of the application of the equation above can be shown for the element A of the MTBE case:

$$W_A^l = \frac{1 * x_1 + 0 * x_2 + 1 * x_3}{(1 * x_1 + 0 * x_2 + 1 * x_3) + (0 * x_1 + 1 * x_2 + 1 * x_3)} = \frac{x_1 + x_3}{x_1 + x_2 + 2x_3} = \frac{x_1 + x_3}{1 + x_3}$$

It is important to underline that the transformation is instantaneous when the direction is from the components to the elements domain; the inverse process requires the solution of the chemical-physical equilibrium system.

## 2.4 CPE model

With all the tools described in the previous pages, it is possible to solve simultaneously the chemical and physical equilibria. Eriksen [18] helps us with two very useful algorithms:

Algorithm 1:

1. Specify the liquid element mole fractions,  $W_j^l$ , and the pressure,  $P$ .  $NE - 1$  element mole fractions need to be specified.
2. Guess the initial values of  $T$  and  $x_i$ .
3. Substitute  $x_i = \sqrt{x_i^2}$  in the following equations to get non-negative values.
4. Use a numerical solver to solve the following system of equations:

- a. The sum of the liquid mole fractions is equal to 1:

$$\sum_{i=1}^{NC} x_i - 1 = 0$$

- b. The sum of the vapour mole fractions is equal to 1 with the modified Raoult's law:

$$\sum_{i=1}^{NC} y_i - 1 = \sum_{i=1}^{NC} \frac{\gamma_i x_i P_i^{sat}}{P} - 1 = 0$$

- c. The liquid element mole fractions are equal to the specified:

$$W_j^l - \frac{\sum_{i=1}^{NC} A_{ji} x_i}{\sum_{k=1}^{NE} \sum_{i=1}^{NC} A_{ki} x_i} = 0, \quad j = 1, 2, \dots, NE - 1$$

- d. The system is at chemical equilibrium:

$$\prod_{i=1}^{NC} (\gamma_i x_i)^{\nu_{ij}} - K_j(T) = 0, \quad j = 1, 2, \dots, NR$$

The system contains  $1 + NE + NR = 1 + NC$  equations with the same number of variables ( $T$  and  $x_1, x_2, \dots, x_{NC}$ ).

5. Calculate the vapour mole fractions for both components and elements with Raoult's modified equation and the following one:

$$W_j^v = \frac{\sum_{i=1}^{NC} A_{ji} y_i}{\sum_{k=1}^{NE} \sum_{i=1}^{NC} A_{ki} y_i}, \quad j = 1, 2, \dots, NE$$

Figure 6: Algorithm 1 proposed by Eriksen to solve the CPE

Algorithm 2:

1. Specify the liquid element mole fraction of one element,  $W_A^l$ , the pressure, P and guess the temperature,  $T_{guess}$ , and the vector of the liquid component molar fraction,  $\mathbf{x}_{guess}$ .
2. Solve the Algorithm 1.
3. Gain the results:  $T, \mathbf{x}, \mathbf{y}, W_A^v$ .
4. Repeat points 1-2-3 for  $0 < W_A^l < 1$ .

Figure 7: Algorithm 2 proposed by Eriksen to draw CPE plots

The two algorithms shown in figure 6 and 7 can be used to generate element-based CPE diagrams. The two graphs below have been generated with the application of the algorithms 1 and 2 for the MTBE reactive system. The operating pressure is 3 atm, the activity coefficients have been evaluated with the Wilson model (Wilson parameter in the appendix), the  $P_{sat}$  is given by the Antoine equation (Antoine parameters in the appendix).

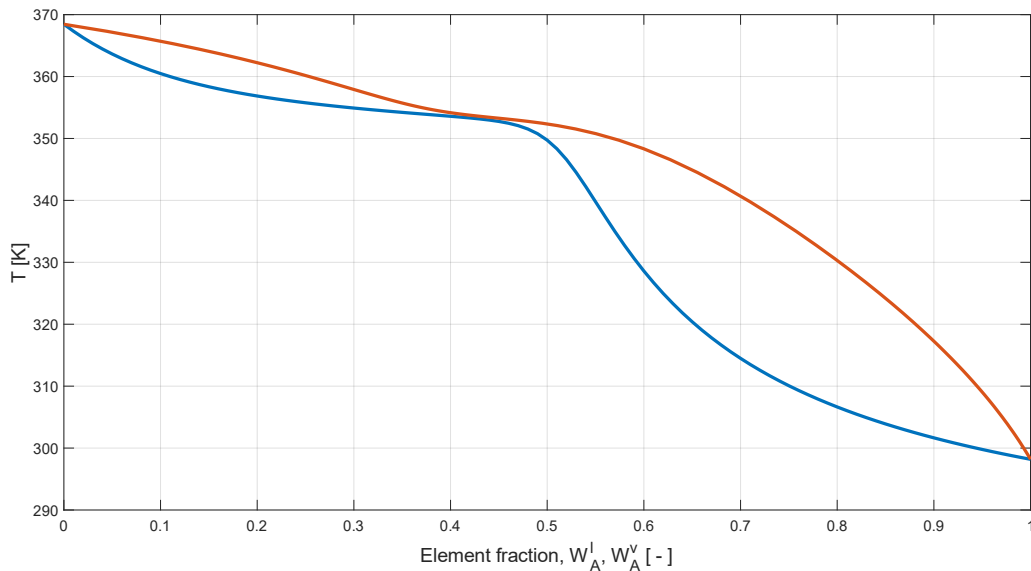


Figure 8: T-WL-WV diagram

The T-W<sup>L</sup>-W<sup>V</sup> diagram (analogous to the Txy diagram for the physical equilibrium) is shown in figure 8. It shows the trends of the dew point and the bubble point of the reactive mixture. It is possible to notice that when  $W_A^l = 0$  ( $x_{CH_3OH} = 1$ ), the boiling point of the pure element B is equal to 337,7 K, while when  $W_A^l = 1$  ( $x_{C_4H_8} = 1$ ), the boiling point of the pure element A is equal to 266,5 K. The two results are consistent with the boiling point of the two pure components.

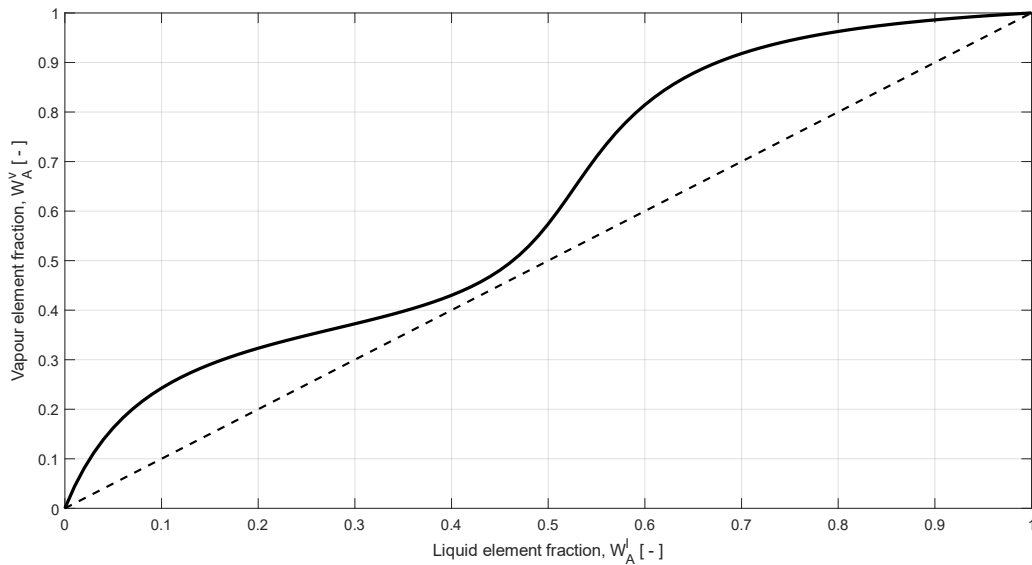


Figure 9: WL-WV plot for the element A

The W<sup>L</sup>-W<sup>V</sup> diagram (analogous to the xy diagram for the physical equilibrium) is shown in figure 9. It shows the relation between the vapour elemental mole fraction of the element A and the liquid elemental mole fraction of the element A when the system is at chemical-physical equilibrium. It is possible to notice that the system presents a reactive azeotrope for  $W_A^l = 0.46$ . It means that it is not possible to go over that point with simple reactive distillation, but the compositions of the two phases are not equal as in a physical azeotrope.

## 3. Methods and algorithms

In this chapter, the algorithms and the methods used to design the reactive and the reactive-cyclic columns will be presented. For the reactive columns, the reactive McCabe-Thiele algorithm and the driving force algorithm will be discussed. For the reactive-cyclic columns, two different approaches will be used: an equilibrium based one and a rate based one.

### 3.1 Reactive Distillation

#### 3.1.1 Design algorithm: reactive McCabe-Thiele

The McCabe-Thiele method is a graphical design algorithm used for the standard separation of binary mixtures [29]. The most important assumption of the method is that in the column the internal vapour and liquid flows remain constant because equal heats of vaporization lead to constant molar overflow. To use this method the feed must be completely specified along with the purity of the top and the bottom products. Using then the xy physical diagram it is possible to move on the equilibrium curve and on the rectifying and stripping lines (the slope of the two lines can be evaluated thanks to mass balances on the column and considering that the q-line depends on the conditions of the feed and it is the locus of the points where the two lines encounter each other) to count the number of equilibrium stages required to perform the separation.

Following the same principle discussed above, it is possible to apply the McCabe-Thiele method also on the  $W^L$ - $W^V$  diagram. The following example is taken from Eriksen [18].

If the following variables are specified:

Table 2: Variables to specify for the column design

$b^F$	1 kmol/s
$W_A^F$	0.70
$W_A^B$	0.50
$W_A^D$	0.99
$RR$	2
$q$	1

it is possible to evaluate the number of the reactive stages needed in a reactive column to gain streams with the desired purity.  $W_A^B$  is set to 0,5 because plotting the component molar fractions as a function of the elemental ones (figure 10), it is clear that at that elemental composition the maximum amount of MTBE should be retrieved after the CPE calculations. The distillate is almost pure isobutene (LK component of the mixture) and the feed is saturated liquid ( $q = 1$ ).

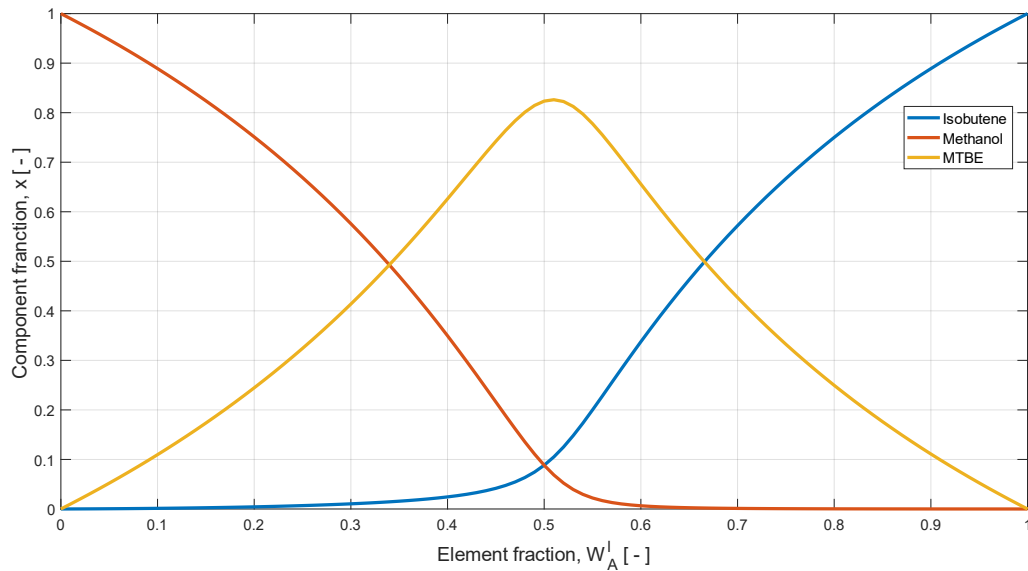


Figure 10: Element Fractions VS Component Fractions



From the steady state elemental balances,

$$b^F = b^B + b^D$$

$$W_A^F b^F = W_A^B b^B + W_A^D b^D$$

It is possible to evaluate the amount of elemental flow for the distillate and the bottom product:

$$b^B = 0.592 \text{ kmol/s}$$

$$b^D = 0.408 \text{ kmol/s}$$

Thanks to the specific of the reflux ratio, it is possible to calculate the liquid flow in the rectifying section and in the stripping section (adding the feed flow rate):

$$b^L = RR * b^D = 0.816 \text{ kmol/s}$$

$$b^{*L} = b^L + b^F = 1.82 \text{ kmol/s}$$

The vapour flow from the reboiler (the \* indicates the stripping section) and the boilup ratio are evaluated as follows (note that the vapour flow in the stripping section is equal to the vapour flow in the rectifying section because the feed is saturated liquid; in the case that there was vapour in the feed, the vapour flows in the two sections would have been different):

$$b^{*V} = b^V = b^{*L} - b^B = 1.22 \text{ kmol/s}$$

$$BR = \frac{b^{*V}}{b^B} = 2.07$$

With all the internal flows evaluated, it is now possible to calculate the slopes of the two working lines of the rectifying and stripping zones:

$$Slope_{rect} = \frac{b^L}{b^V} = 0.667$$

$$Slope_{str} = \frac{b^{*L}}{b^{*V}} = 1.48$$

The two working lines start on the specified distillate and bottom compositions. The number of theoretical stages can be evaluated drawing steps from the working lines to the equilibrium

curve, starting from the bottom composition (the desired product is MTBE that exits from the reboiler of the column). The plot shows that 6 theoretical reactive stages are necessary to obtain the desired products with the desired purity. It is necessary to recall that the reboiler is an equilibrium stage, so it is included in the plot, while the condenser is not, so at the end, the final design comprehend a column with 5 theoretical trays, the partial reboiler and the total condenser. The feed should be positioned on the second tray from the bottom (reboiler excluded). The graphical procedure is shown in figure 11.

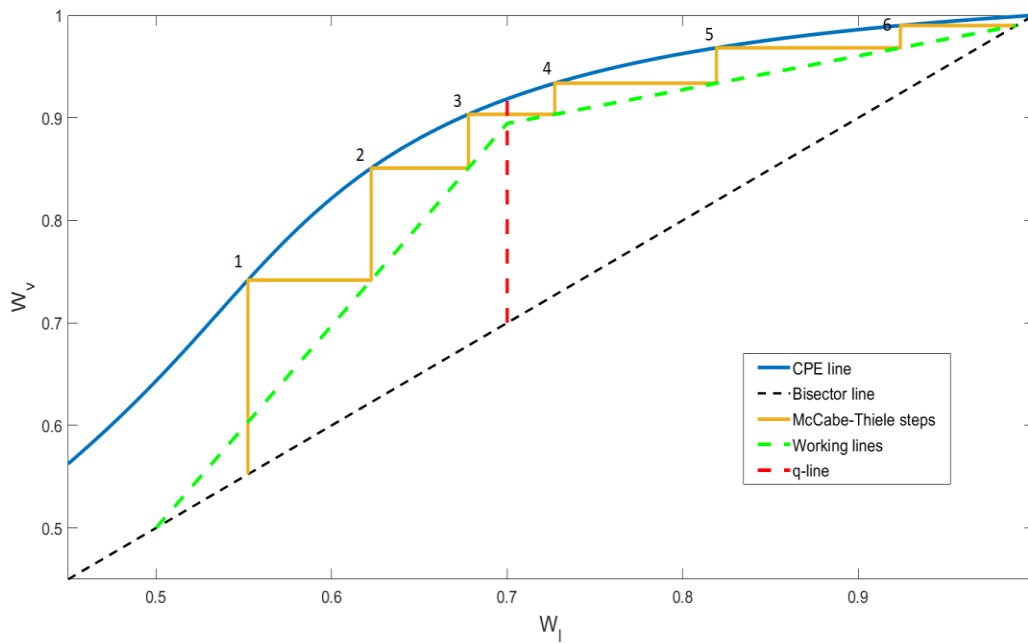


Figure 11: McCabe-Thiele for a reactive column

### 3.1.2 Expansion to multi-element systems

As stated in Nielsen work [30], Jantharasuk et al. [31] proposed a procedure to apply the CPE also to those systems that are not binary and present more than two elements. The concept is to enlighten the equivalent element composition by choosing the light key element (LK) and the heavy key element (HK) and evaluating the following quantities:

$$W_{eq,LK} = \frac{W_{LK}}{W_{LK} + W_{HK}}$$

$$W_{eq,HK} = \frac{W_{HK}}{W_{LK} + W_{HK}}$$

The two quantities above represent the compositions of the equivalent light key element and the equivalent heavy key element; this transformation takes with it the hypothesis that all the non-key elements would have little to no effect on the reactive separation of the key elements, so the amount of non-key element can be set to an arbitrary and constant amount throughout the column. After the plot of the equivalent operating lines, Jantharasuk et al would then graphically determine the number of stages, just as the binary case presented above.

### 3.1.3 Driving force design algorithm

The driving force concept was firstly applied on continuous distillation by Gani and Bek-Pedersen [32]. The driving force is defined as the absolute value of the difference between the composition of the vapour and the liquid phase for the light key component of the column:

$$FD_{LK} = |y_{LK} - x_{LK}|$$

The separation will be easier when the driving force is higher; a null value of the driving force corresponds to a physical azeotrope.

The same concept can be extended also to reactive systems if we change a bit the definition and we consider not the component molar fractions, but the element ones:

$$FD_{LK} = |W_{LK}^v - W_{LK}^l|$$

The implications that a higher driving force corresponds to a simpler separation and  $FD_{LK} = 0$  means that we are in the presence of an azeotrope remain equal to the ones formulated for the non-reactive system.

Once plotted driving force VS  $W_{LK}^l$ , it is possible to gain from the graph some important parameters that will be useful in the design phase: connecting the points corresponding to the

desired product compositions (top and bottom) with the point with the maximum driving force, it is possible to evaluate the minimum reflux ratio and the minimum boilup ratio by calculating the slopes of these two lines. The two minimum values can then be increased to make the separation feasible and optimally carried out.

To operate always at the maximum driving force, it is then necessary to evaluate the optimal  $q$  thanks to the following equation:

$$q = RR * \frac{W_F^l - D_x}{D_x - W_D^l} + \frac{W_F^l - W_D^l}{D_x - W_D^l}$$

With all these values, it is then possible to perform the McCabe-Thiele procedure on the driving force diagram to count the number of theoretical trays necessary to carry out the reactive separation, but this time it will be guaranteed that each step will be done at the maximum possible driving force. The graphical procedure is shown in figure 12.

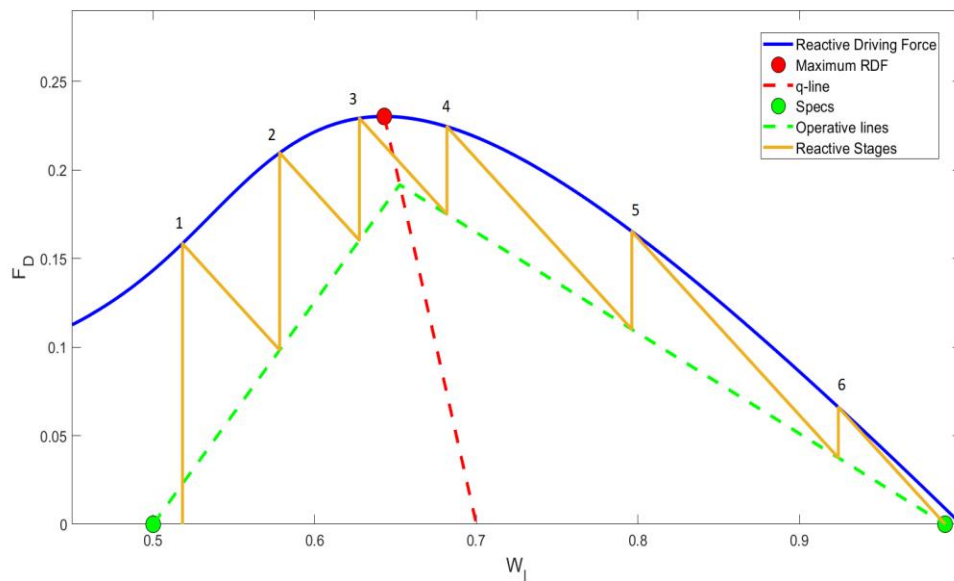


Figure 12: McCabe-Thiele procedure performed on the driving force diagram

The major improvement introduced by this method is that it is sure that at the end of the design the column will operate with the lowest possible amount of energy requested by the reboiler and

provided by the condenser (it is always minimized the sum  $RR + BR$ ) [30]. The major drawback is that to guarantee the optimal  $q$ , if the feed mixture is liquid, it should be heated before entering the column to be partially vaporized and meet the specific  $q$  required.

## 3.2 Reactive-Cyclic Distillation

### 3.2.1 Equilibrium based approach

The equilibrium based approach, as the name suggests, can be used when in a cyclic reactive column, chemical equilibrium can be assumed. Eriksen [18] assumes a constant elemental vapour flow throughout the column and that all the stages are reactive, also the reboiler. The algorithm has been summed up by Nielsen as follows (figure 13):

1. Fix the target bottoms element composition, element external flowrates per cycle  $b^F, b^B$  and  $b^B$  and the feed composition  $W^F$ .
2. Fix the element vapour flow rate per cycle  $b^V * t_{vap}$ .
3. Fix the reboiler holdup at the end of the VFP:  $b_1^{H,(V)}$ .
4. Run the backwards-integration, starting from the specified bottom element compositions.
5. Add stages in the backwards-integration method until the tray liquid element composition matches the composition in the feed. Then the next tray is assigned to be the feed tray.
6. Add stages in the backwards-integration method until the tray liquid element composition matches the design distillate target composition. Then, the number of needed reactive stages is the number of stages plus one (the condenser).

Figure 13: Eriksen algorithm (adapted by Nielsen) to design a reactive-cyclic column

The algorithm can be seen as a sum of the one suggested by Pătruț et al. for the pure cyclic distillation [33] and the one suggested by Pérez Cisneros et al. to calculate simultaneously the chemical and vapor-liquid equilibria [34].

The elemental balance equations for the equilibrium based design proposed by Eriksen [18] are reported below (figure 14);  $b^H$  is the element holdup on each stage and  $b^B$ ,  $b^D$ ,  $b^F$ ,  $b^V$  are the bottom, distillate, feed and vapour element flows, respectively.

Vapour flow period	
Reboiler: $\frac{db_{1,i}^H}{dt} = -b^V * W_{1,i}^v$	for $i = 1, \dots, NC$
Trays: $\frac{db_{k,i}^H}{dt} = b^V * (W_{k-1,i}^v - W_{k,i}^v)$	for $i = 1, \dots, NC, k > 2$
Liquid flow period	
Reboiler: $b_{1,i}^{H,(L)} = b_{1,i}^{H,(V)} - b^B * W_{1,i}^{L,(V)} + b_{2,i}^{H,(V)}$	for $i = 1, \dots, NC$
Feed tray: $b_{NF-1,i}^{H,(L)} = b_{NF,i}^{H,(V)} + b^F * W^F$	for $i = 1, \dots, NC$
Other trays: $b_{k,i}^{H,(L)} = b_{k+1,i}^{H,(V)}$	for $i = 1, \dots, NC$

Figure 14: Elemental mass balances for Eriksen CPE driven algorithm

The above reported equations must be integrated with the backwards-integration method starting from the reboiler: Eriksen would start by specifying the element vapour flow, bottoms, feed and distillate flow rates per cycle and lastly also the feed and the target product compositions. Then starting from the specified bottom compositions, the algorithm would integrate the mass balances for each component backwards in time, use the liquid flow period mass balances to calculate the holdup of the stage above and then integrate once again the vapour flow period balances back in time until the specified distillate composition would be obtained. The feed then would be introduced where the element composition most resembles the feed composition.

### 3.2.1.1 Expanded design algorithm

The algorithm presented in the paragraph 3.1 has been furtherly expanded by Nielsen [30] to include the possibility of working with multi-element systems, to accommodate the multi-feed cases and to account for feeds with a quality of  $q \neq 1$ . The key change introduced to make all this possible is that the feed does not enter anymore in the column during the VFP, but during the LFP: this has been introduced because introducing a liquid stream during the VFP, would result in an unwanted liquid draining when working with trays like the Maleta ones [22] that have vapour-flow controlled pistons.

Figure 15, figure 16, figure 17 and figure 18 show respectively the expanded mass balances of the algorithm (for VFP and LFP), the procedure for the preliminary screening of the elements used to choose the operating area and the expanded algorithm.

Vapour flow period

$$\text{Reboiler: } \frac{db_{1,i}^H}{dt} = -b_1^V * W_{1,i}^v \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Trays: } \frac{db_{1,i}^H}{dt} = b_{k-1}^V * W_{k-1,i}^v - b_k^V * W_{k,i}^v \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Condenser: } \frac{db_{k,NT}^H}{dt} = b^V * W_{NT-1,i}^v \quad \text{for } i = 1, \dots, \text{NC}$$

where the vapour flow for each tray is defined as:

$$b_k^V = b_{k-1}^V \quad \text{for } k \neq \text{NF}$$

$$b_k^V = b_k^V + b^{VF} \quad \text{for } k = \text{NF}$$

assuming constant elemental heat of vaporization, independent of element composition. Note that the feed tray definition is different the one used by Pătruț et al [35] and Eriksen [18], as the feed is introduced on the stage where it is also exposed to its first vapour flow period.

Figure 15: Elemental VFP mass balances for Nielsen expanded algorithm

Liquid flow period

$$\text{Reboiler: } b_{1,i}^{H,(L)} = b_{1,i}^{H,(V)} - b^B * W_{1,i}^{L,(V)} + b_{2,i}^{H,(V)} \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Feed tray(s): } b_{NF,i}^{H,(L)} = b_{NF+1,i}^{H,(V)} + b^F * W_i^F \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Tray below condenser: } b_{NT-1,i}^{H,(L)} = b^L * W_{NT,i}^{L,(V)} \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Condenser: } b_{NT,i}^{H,(L)} = b_{NT,i}^{H,(V)} - (b^L + b^D) * W_{NT,i}^{L,(V)} \quad \text{for } i = 1, \dots, \text{NC}$$

$$\text{Other trays: } b_{k,i}^{H,(L)} = b_{k+1,i}^{H,(V)} \quad \text{for } i = 1, \dots, \text{NC, } k \neq \text{NF}$$

Figure 16: Elemental LFP mass balances for Nielsen expanded algorithm

1. Find the light key, heavy key and non-key elements, using the rules stated by Jantharasuk et al. [31], for the given reactive mixture.
2. Fix the non-key element compositions and calculate the reactive bubble point, using the algorithm 2 of Eriksen reported in Figure 7.
3. Plot the equivalent phase diagram, using:  $W_{eq,LK} = \frac{W_{LK}}{W_{LK} + W_{HK}}$
4. Identify any reactive azeotropes, choose the operating area and finally fix the equivalent element compositions of bottom, feed and distillate streams.
5. Specify the complete bottoms element composition, using the chosen equivalent composition.

Figure 17: Preliminary procedure to find the LK and the HK elements and to choose the operative area



1. Fix the complete target bottoms element composition, element external flow-rates per cycle  $b^F, b^D, b^B$  and the feed quality and composition  $q$  and  $W^F$ .
2. Fix the element vapour flow rate from the reboiler per cycle  $b^V * t_{vap}$ .
3. Fix the reboiler holdup at the end of the VFP:  $b_1^{H,(V)}$ .
4. Run the backwards-integration, starting from the specified bottoms element composition.
5. Run the backwards-integration method until the tray liquid element composition matches the composition in a given feed (equivalent element composition if multi-element). Then, the next tray is assigned to be that specific feed tray. In case of multiple individual feeds (that are not located in the boundaries of the equivalent element operating area), return to 5 until all feeds have been located.
6. Add stages in the backwards-integration method until the tray liquid element composition matches the design distillate target composition (equivalent element composition if multi-element). Then, the number of needed reactive stages is the number of stages plus one (the condenser).

Figure 18: Nielsen Expanded CPE driven algorithm

### 3.2.2 Rate based approach

The equilibrium based approach is very useful when the reaction involved is intrinsically fast. Dealing with a slow reaction needs instead a different approach because assuming that the equilibrium is reached on each tray can lead to sub-dimensioning the reactive cyclic towers.

Pătruț et al. [35] proposed a rate based design algorithm that resembles the one used for pure cyclic distillation [33] and that uses the backwards-integration as the equilibrium based one.

It is assumed that the column presents three distinct zones: a rectifying zone, a reactive zone and a stripping zone. The catalyst is loaded only on the reactive trays and the algorithm is able to directly evaluate the number of the stripping stages alongside with the number of reactive trays.

The variables that have to be specified before running the algorithm are the following: the desired conversion, product purities, feed flow and composition, the external vapour flow and the duration of the vapour flow period. With these variables, it is possible to evaluate the preliminary mass balances to obtain the bottoms and distillate flows. After that, the backwards-integration algorithm is used to go up in the column from the reboiler to a point where there is no more change in tray composition from a tray to the one immediately above.

Given the number of non-reactive stripping stages, Pătruț et al. would assume the top one as a reference to take the useful data (tray composition and temperature) to evaluate a predicted mean reaction rate (on catalyst mass basis) using a provided reaction rate expression. The number of reactive trays would be then calculated from the following expression (assuming a fixed amount of catalyst on each tray):

$$N_{cat} = \frac{m_{cat}}{m_{tray,cat}} = \frac{F * \xi}{r_{av} * m_{tray,cat}}$$

The number of rectifying stages would then be found by trial and error by simulating the column until the target distillate composition and the specified conversion are reached. The algorithm and the reactive-cyclic mass balances are presented in the following figures (figure 19 and figure 20):

1. Specify conversion  $\xi$ , feed  $x_F$  and  $F$ , design objective product purities  $x_B$  and  $x_D$  and the vapour flow period duration  $t_{vap}$  and flow magnitude coming from the reboiler  $V$ .
2. Calculate bottoms and distillate flow rates based on component mass balances over the complete column.
3. Run backwards-integration for stripping section until the composition on each tray approaches a constant composition asymptotically. This number of stages is set to be the number of stripping stages (including reboiler).
4. Calculate the reaction rate based on the tray composition of the last added stripping section stage. This will here be assumed to be equal to the average reaction rate on each reactive stage.
5. Specify catalyst loading on each tray and estimate the number of reactive stages using the following equation: 
$$N_{cat} = \frac{m_{cat}}{m_{tray,cat}} = \frac{F \cdot \xi}{r_{av} \cdot m_{tray,cat}}$$
6. Add a non-reactive condenser and carry out a rigorous simulation until pseudo steady state.
7. Check if the conversion and the specified product purities are obtained. If they are, the design has been obtained. If not, adjust the number of non-reactive stages above the reactive section and return to 7.

Figure 19: Pătruț et al. rate based algorithm

Vapour flow period

$$\begin{aligned} \text{Reboiler: } \frac{dH_{1,i}}{dt} &= -V_1 * y_{1,i} && \text{for } i = 1, \dots, \text{NC} \\ \text{Trays: } \frac{dH_{k,i}}{dt} &= V_{k-1} * y_{k-1,i} - V_k * y_{k,i} + v_i * r_k * m_k && \text{for } i = 1, \dots, \text{NC} \\ \text{Condenser: } \frac{dH_{NT,i}}{dt} &= V_{NT-1} * y_{NT-1,i} && \text{for } i = 1, \dots, \text{NC} \end{aligned}$$

where the varying vapour flow rate is described using the simplified energy balance:

$$V_k = \frac{V_{k-1} * \sum_i \lambda_{k,i} * y_{k-1,i} + r_k * m_k * \Delta^r H_k}{\sum_i \lambda_{k,i} * y_{k,i}}$$

where  $\lambda_i$  is the heat of vaporization for each component,  $r_k$  is the reaction rate,  $\Delta^r H_k$  is the heat of reaction and  $m_k$  is the mass of catalyst.

Liquid flow period

$$\begin{aligned} \text{Reboiler: } H_{1,i}^{(L)} &= H_{1,i}^{(V)} - B * x_{1,i}^{(V)} + H_{2,i}^{(V)} && \text{for } i = 1, \dots, \text{NC} \\ \text{Feed tray: } H_{NF-1,i}^{(L)} &= H_{NF,i}^{(V)} + F * x_{F,i}^{(V)} && \text{for } i = 1, \dots, \text{NC} \\ \text{Tray below condenser: } H_{NT-1,i}^{(L)} &= L * x_{NT,i}^{(V)} && \text{for } i = 1, \dots, \text{NC} \\ \text{Condenser: } H_{NT,i}^{(L)} &= H_{NT,i}^{(V)} - (D + L) * x_{NT,i}^{(V)} && \text{for } i = 1, \dots, \text{NC} \\ \text{Other trays: } H_{k,i}^{(L)} &= H_{k+1,i}^{(V)} && \text{for } i = 1, \dots, \text{NC} \end{aligned}$$

Figure 20: Reactive-cyclic mass balances by Pătruț et al.

For comparison purposes, alongside the design obtained with the algorithm, Nielsen [30] generated a design with the minimum number of stages. This benchmark design has been obtained simply by trial and error of the number of stripping, reactive and rectifying stages, but still constrained with the same design objectives as the ones used in the Pătruț et al. [35] algorithm. For the rest of the thesis work, this design will be denoted as the minimum design.

## 4. Case studies

In this chapter, the application of the algorithms presented in chapter 3 will be presented alongside the results obtained for the two case studies.

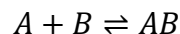
### 4.1 Case study 1: Fast reaction, the MTBE case

The MTBE synthesis is a good example of fast reaction. It has been chosen among the others because it has been widely studied both for reactive distillation and for reactive-cyclic distillation. In this paragraph the conditions of the feed, the design objectives and the properties of the reactive mixture will be presented.

The feed is composed of isobutene (A) and methanol (B) with a molar ratio of 0,7:0,3. It is decided to work with an excess of A because it is more easily separated from the reactive mixture than methanol. The target of both the columns will be to obtain almost pure isobutene as distillate and a mixture of almost pure MTBE and unreacted methanol as bottom products. The heat of reaction is a “good friend” of this configuration: as the reaction is exothermic, it is possible to use part of the heat of reaction to reduce the amount of heat that must be provided to the reboiler.

The Wilson equation will be used both for the periodic case and for the non periodic one and an ideal vapour phase is assumed. In the appendix it is possible to find all the coefficients of the Wilson equation and the correlation used to evaluate the equilibrium constant (Barbosa and Doherty [36]).

In both cases the system will be studied in the element domain; as it is shown in chapter 2.3, it is possible to write the MTBE reaction as:



where A represents  $C_4H_8$  and B represents  $CH_3OH$ , and so the resulting formula matrix appears to be:

$$A = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \end{bmatrix}$$

In the following paragraphs it is possible to give a look to the design specifications for the two cases and design and simulation results.

#### 4.1.1 MTBE: Reactive distillation

The design specifications for the MTBE reactive case are resumed in the following table 3:

*Table 3: Design specifications for MTBE reactive column*

<i>Pressure [atm]</i>	$W_A^F$	$W_A^D$	$W_A^B$	<i>Catalyst</i>	<i>Catalyst amount [mol/L]</i>
3	0,7	0,99	0,5	$H_2SO_4$	1

The pressure in the column is set to 3 atm to make sure that is possible to use cooling water in the condenser. Plotting the component molar fraction as a function of the elemental molar fraction (figure 10) it is clear that to gain the maximum amount of MTBE, the elemental molar fraction of the bottom product has to be set to 0,5.

The distillate elemental molar fraction is chosen considering that almost pure isobutene is asked to be distilled from the top of the column, that is why  $W_A^D = 0,99$ .

Once chosen the area included between  $W_A = 0,5$  and  $W_A = 0,99$  it is then possible to use the algorithm described in chapter 2 to design the reactive zone of the column.

The column has been then simulated on Aspen HYSYS and dimensioned with the correlations proposed in the appendix; in the following table 4 it is possible to have a look at the final results:

Table 4: MTBE reactive columns. Simulation results

	Unit of measure	Column 1: Reactive tower, $h_T = 12$ in	Column 2: Reactive tower, $h_T = 18$ in	Column 3: Reactive tower, $h_T = 24$ in
Conversion	[-]	0,9867	0,9867	0,9867
Rectifying Stags	[-]	13	13	13
Reactive Stages	[-]	3	3	3
Stripping Stages	[-]	15	15	15
Feed stage [from bottom]	[-]	16	16	16
$q$	[-]	1	1	1
$F$	[kmol/s]	0,01	0,01	0,01
$D$	[kmol/s]	0,0041	0,0041	0,0041
$B$	[kmol/s]	0,0030	0,0030	0,0030
$V$	[kmol/s]	0,0027	0,0027	0,0027
$L$	[kmol/s]	0,0039	0,0038	0,0038
$RR$	[-]	0,951	0,948	0,948
$BR$	[-]	0,900	0,896	0,896
$zF$	[-]	[0,7; 0,3; 0]	[0,7; 0,3; 0]	[0,7; 0,3; 0]
$xD$	[-]	[0,9932; 0,0068; 0]	[0,9932; 0,0068; 0]	[0,9932; 0,0068; 0]
$xB$	[-]	[0,0059; 0,0041; 0,99]	[0,0059; 0,0041; 0,99]	[0,0059; 0,0041; 0,99]
$xB_{MTBE}$	[-]	0,99	0,99	0,99
Hole area	[-]	3%	4%	4%
Column Diameter	[m]	0,51	0,45	0,4
Column Height	[m]	13,8	18,3	22,7
$Q_c$	[kW]	165,6	165,6	165,6
$Q_r$	[kW]	71	71	71

The column has been simulated with three different tray spacings because in the following chapter, a cost analysis will be performed on the different configurations described in this chapter.

#### 4.1.2 MTBE: Reactive-Cyclic distillation

The design specifications for the MTBE reactive-cyclic case are resumed in the following table 5:

Table 5: Design specifications for MTBE reactive-cyclic column

Pressure [atm]	$W_A^F$	$W_A^D$	$W_A^B$	$t_{vap}$ [s]	Catalyst	Catalyst amount [mol/L]
3	0,7	0,99	0,5	10	$H_2SO_4$	1

The pressure in the column is set to 3 atm to make sure that is possible to use cooling water in the condenser. The specifications regarding the top and the bottom products have been taken from the study performed on the reactive distillation in the previous paragraph. As the reaction is quite fast, the period of the VFP is set to 10 s.

The algorithm based on CPE presented in chapter 3, requires the specification of the initial holdup of the reboiler and the flow of vapour coming from the reboiler each cycle; these two data are presented in the following table 6:

Table 6: Additional design specifications for MTBE reactive-cyclic column

	Initial holdup [kmol/cycle]	$V * t_{vap}$ [kmol/cycle]
$q = 1$	0,060	0,061
$q = 0,7524$	0,0531	0,047



There are little differences between the design made with the feed at bubble point ( $q = 1$ ) and the one sent in the column to operate at the maximum driving force; the equations used to evaluate the two data, are the following:

$$M_0 = W_A^B * (b_L + q * b_F)$$

$$V * t_{vap} = b_D * (1 + R) - b_F * (1 - q)$$

Both the equations can be retrieved after solving the mass balances on the whole column and using the driving force diagram as a base: after finding the minimum reflux ratio, it is possible to increase it and use the graphical method to find all the useful data such as the slopes of the working lines, the boilup ratio and the amount of vapour exiting from the reboiler. In figure 21 it is reported an example of graphical evaluation of the slopes of the working lines corresponding to the condition of minimum reflux.

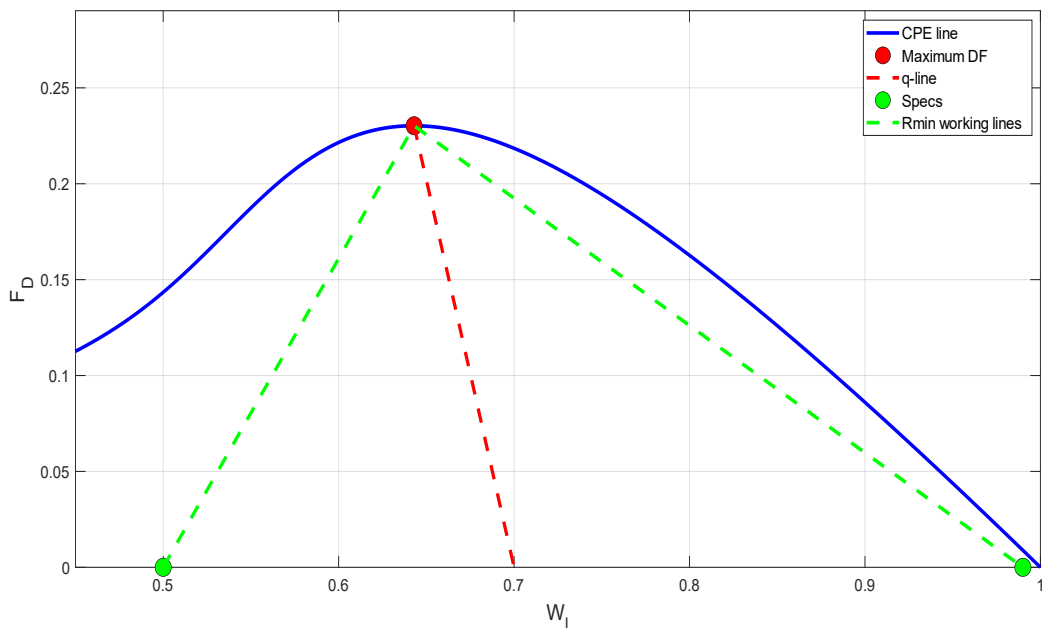


Figure 21: Driving force diagram with working lines corresponding to the minimum reflux ratio

The column has been then simulated on MATLAB until reaching a pseudo steady state and dimensioned with the correlations proposed in the appendix; in the following table 7 it is possible to have a look at the final results:

Table 7: MTBE reactive-cyclic columns. Simulation results

	Unit of measure	Column 4: $t_{vap} = 10s, q1$	Column 5: $t_{vap} = 10s, q@DF$	Column 6: $t_{vap} = 1s, q@DF$
Conversion	[-]	0,9929	0,9947	0,9939
Rectifying Stages	[-]	1	1	0
Reactive Stages	[-]	3	3	5
Stripping Stages	[-]	3	3	3
Feed stage [from bottom]	[-]	5	5	6
$q$	[-]	1	0,7524	0,7524
$F$	[kmol/cycle]	0,1	0,1	0,1
$D$	[kmol/cycle]	0,0403	0,0403	0,0403
$B$	[kmol/cycle]	0,0299	0,0299	0,0299
$V*t_{vap}$	[kmol/cycle]	0,061	0,047	0,047
$t_{vap}$	[s]	10	10	1
$t_{liq}$	[s]	0	0	0
$L$	[kmol/cycle]	0,1094	0,0882	0,0882
$RR$	[-]	2,7154	2,1882	2,1877
$BR$	[-]	2,0397	1,5722	1,571
$zF$	[-]	[0,7; 0,3; 0]	[0,7; 0,3; 0]	[0,7; 0,3; 0]
$xD$	[-]	[0,9972; 0; 0,0028]	[0,9963; 0; 0,0037]	[0,9972; 0; 0,0028]
$xB$	[-]	[0,0006; 0,007; 0,9924]	[0,0014; 0,0067; 0,9919]	[0,0009; 0,0079; 0,9912]
$x_{BMTBE}$	[-]	0,9924	0,9919	0,9912

		Pseudo Sulfuric	Pseudo Sulfuric	Pseudo Sulfuric
<i>Catalyst</i>	[-]	Acid	Acid	Acid
<i>Catalyst amount</i>	[mol/L]	1	1	1
<i>Hole area</i>	[-]	6%	6%	6%
<i>Column Diameter</i>	[m]	0,34	0,29	0,29
<i>Column Height</i>	[m]	8	8	8,6
<i>Q<sub>c</sub></i>	[kW]	303,8	260,8	2606,8
<i>Q<sub>r</sub></i>	[kW]	155,1	119,5	1195,1

In table 7 it is possible to look at three different cases: the first two columns (Column 4 and 5) differ from the third because of the duration of the VFP, the third (Column 6) has been designed and simulated for the sake of curiosity and to understand how much the reaction is fast: it is really hard from a physical point of view to operate with a  $t_{vap}$  of 1 second, but in theory it should be possible to guarantee the same conversion adding just 2 reactive stages. Another issue when working with 1 second of duration of the VFP could be that the reboiler and the condenser should be too big because of the enormous amount of heat that must be provided in the first and removed from the second.

Between column 4 and 5 there are not so many differences, but the most important one is that in column 5 the heat that should be provided to the reboiler and the heat that should be removed from the condenser are (as expected) lower than the ones of the column 4 that does not work at the maximum driving force. It is necessary to point out that to work at the maximum DF the feed should be preheated; there must be a further analysis to understand if the heat saved in the column is or is not greater than the one that must be provided to preheat the feed before entering the column.

## 4.2 Case study 2: Slow reaction, the MeOAc case

The Methyl Acetate synthesis is a good example of slow reaction. It has been chosen among the others because it has been widely studied above all for reactive distillation. In this paragraph the conditions of the feed, the design objectives and the properties of the reactive mixture will be presented.

The feed is composed of acetic acid (A) and methanol (B) in stoichiometric proportions. Usually, conventionally operated reactive columns producing MeOAc are designed with two feeds: pure A at the top reactive stage and pure B at the last reactive stage. Also in this work, this configuration will be used. The target of the separation will be the one to obtain almost pure methyl acetate from the top stream and almost pure water from the bottom one. It is chosen to work with reactive distillation because methyl acetate forms two low-boiling azeotropes: one with water ( $x_{MeOAc} = 0.92$ ) and one with methanol ( $x_{MeOAc} = 0.67$ ); the difficulties in the downstream separations can be significantly avoided using reactive (or reactive-cyclic) distillation.

The NRTL equation will be used both for the periodic case and for the non periodic one and an ideal vapour phase is assumed. In the appendix it is possible to find all the coefficients of the NRTL equation and the correlation used to evaluate the equilibrium constant (Zuo et al. [37]).

### 4.2.1 MeOAc: Reactive distillation

The design specifications for the MTBE reactive case are resumed in the following table 8:

Table 8: Design specifications for MeOAc reactive column

Pressure [atm]	$z_F(\text{total})$	$x_{MeOAc}^D$	Conversion	Catalyst	Catalyst amount [kg]
1	[0,5; 0,5]	0,95	> 90%	NKC-9	25

The pressure in the column is set to 1 atm because even in these conditions it is possible to use cooling water in the condenser. The reactive case has been taken from Huss et al. study [38] and readapted to reach the same productivity and purity of the reactive-cyclic ones.

In the following table 9 it is possible to see the results of the simulation of the column on Aspen HYSYS with three different tray spacings. It was not possible to dimension column 7: none of the feasible combinations diameter/hole area could avoid both weeping and flooding in the column.

Table 9: MeOAc reactive columns. Simulation results

	Unit of measure	Column 7: Reactive tower, $h_T = 12$ in	Column 8: Reactive tower, $h_T = 18$ in	Column 9: Reactive tower, $h_T = 24$ in
Conversion	[-]	0,9731	0,9731	0,9732
Rectifying Stags	[-]	2	2	2
Reactive Stages	[-]	33	33	33
Stripping Stages	[-]	3	3	3
Feed stage [from bottom]	[-]	[13; 36]	[13; 36]	[13; 36]
$q$	[-]	[1; 1]	[1; 1]	[1; 1]
$F$	[kmol/s]	[0,004167; 0,004167]	[0,004167; 0,004167]	[0,004167; 0,004167]
$D$	[kmol/s]	0,004125	0,004125	0,004125
$B$	[kmol/s]	0,004208	0,004208	0,004208
$V$	[kmol/s]	0,004064	0,004064	0,004064
$L$	[kmol/s]	0,004357	0,004357	0,004357
$RR$	[-]	1,056	1,056	1,057
$BR$	[-]	0,966	0,966	0,966
$zF$	[-]	[0; 1; 0; 0]	[0; 1; 0; 0]	[0; 1; 0; 0]
	[-]	[1; 0; 0; 0]	[1; 0; 0; 0]	[1; 0; 0; 0]

$x_D$	[-]	[0,0148; 0; 0,95; 0,0352]	[0,0148; 0; 0,95; 0,0352]	[0,0149; 0; 0,95; 0,0351]
$x_B$	[-]	[0,0122; 0,0267; 0,0322; 0,9289]	[0,0122; 0,0267; 0,0322; 0,9289]	[0,0122; 0,0267; 0,0322; 0,9289]
Hole area	[-]	*	10%	10%
Column Diameter	[m]	*	0,537	0,52
Column Height	[m]	15,97	21,46	26,95
$Q_c$	[kW]	262,5	262,5	262,5
$Q_r$	[kW]	146,7	146,7	146,7

#### 4.2.2 MeOAc: Reactive-Cyclic distillation

The design specifications for the MeOAc reactive-cyclic case are resumed in the following table 10:

Table 10: Design specifications for MeOAc reactive-cyclic column

Pressure [atm]	$z_F$	$x_{MeOAc}^D$	$x_{AcOH}^D$	$t_{vap}$ [s]	Catalyst	Catalyst amount [kg]
1	0,5	> 0,95	< 0.005	120	NKC-9	25

The column has been designed thanks to the algorithm by Pătruț et al. [35] presented in chapter 3.

The reaction scheme is the following:



with  $\Delta H^r = -3016,5 \text{ kJ/kmol}$ .

The rate expression used to model the reaction was derived by Zuo et al. [37], it is based on the acidic cation-exchange resin NKC-9 and it is reported in the appendix.

The algorithm has been run with the code proposed by Nielsen [30]. The results obtained are similar to the one shown in his work: Pătruț et al. algorithm hugely overestimates the number of trays because the backwards-integration method estimates a really low amount of reactants on each tray. That is why also in this work we will continue talking about the minimum design obtained simply by trial and error on the number of reactive, rectifying and stripping stages.

In the following table 11 it is possible to see the results obtained from the simulation on MATLAB of the column until pseudo steady state is reached:

Table 11: MeOAc reactive-cyclic columns. Simulation results, base case

	Unit of measure	Column 10
<i>Conversion</i>	[-]	0,8862
<i>Rectifying Stags</i>	[-]	5
<i>Reactive Stages</i>	[-]	17
<i>Stripping Stages</i>	[-]	4
<i>Feed stage [from bottom]</i>	[-]	[5; 22]
<i>q</i>	[-]	1
<i>F</i>	[kmol/cycle]	[0,5; 0,5]
<i>D</i>	[kmol/cycle]	0,495
<i>B</i>	[kmol/cycle]	0,505
<i>V*tvap</i>	[kmol/cycle]	1,1
<i>tvap</i>	[s]	120
<i>tliq</i>	[s]	0
<i>L</i>	[kmol/cycle]	0,934
<i>RR</i>	[-]	1,8868
<i>BR</i>	[-]	2,1783
<i>zF</i>	[-]	[0; 1; 0; 0]

	[-]	[1; 0; 0; 0]
$x_D$	[-]	[0; 0,0398; 0,8949; 0,0653]
$x_D$ (MeOAc)	[-]	0,8949
$x_B$	[-]	[0,1128; 0,0736; 0; 0,8136]
Catalyst	[-]	NKC-9
Catalyst amount	[kg]	25
Hole area	[-]	3%
Column Diameter	[m]	0,68
Column Height	[m]	19,4
$Q_c$	[kW]	363,9
$Q_r$	[kW]	373,2

The results proposed in the table show that with a vapour flow period time of 120 seconds, the specifications are not reached: the conversion is less than 90% just like the purity of the desired product.

To overcome this problem, two different approaches have been used:

1.  $t_{vap}$  modification;
2.  $t_{liq}$  modification.

#### 4.2.2.1 $t_{vap}$ modification

The column has been simulated reducing and increasing the VFP: reducing the duration of the vapour flow period is not a feasible option because in this situation, the reaction does not have the time to reach a suitable conversion; increasing  $t_{vap}$  is instead dangerous because the vapour from the reboiler could be too little, thus bringing the column into a weeping condition. In the following tables it is possible to see the results of the simulations of the minimum design column but with different  $t_{vap}$ .  $t_{vap}$  has been reduced to a quarter (30 s), a third (40 s) and a half (60 s) and increased to five quarters (150 s) and three halves (180 s).



Table 12: MeOAc reactive-cyclic columns. Simulation results, smaller duration of VFP

	Unit of measure	Column 11, $t_{vap} = 30\text{ s}$	Column 12, $t_{vap} = 40\text{ s}$	Column 13, $t_{vap} = 60\text{ s}$
Conversion	[-]	0,6866	0,7378	0,7997
Rectifying Stags	[-]	5	5	5
Reactive Stages	[-]	17	17	17
Stripping Stages	[-]	4	4	4
Feed stage [from bottom]	[-]	[5; 22]	[5; 22]	[5; 22]
$q$	[-]	1	1	1
$F$	[kmol/cycle]	[0,5; 0,5]	[0,5; 0,5]	[0,5; 0,5]
$D$	[kmol/cycle]	0,495	0,495	0,495
$B$	[kmol/cycle]	0,505	0,505	0,505
$V \cdot t_{vap}$	[kmol/cycle]	1,1	1,1	1,1
$t_{vap}$	[s]	30	40	60
$t_{liq}$	[s]	0	0	0
$L$	[kmol/cycle]	0,764	0,7925	0,8328
$RR$	[-]	1,5435	1,601	1,6823
$BR$	[-]	2,1784	2,1784	2,1784
$z_F$	[-]	[0; 1; 0; 0]	[0; 1; 0; 0]	[0; 1; 0; 0]
	[-]	[1; 0; 0; 0]	[1; 0; 0; 0]	[1; 0; 0; 0]
$x_D$	[-]	[0,0123; 0,1277; 0,6936; 0,1664]	[0,0084; 0,0927; 0,7453; 0,1536]	[0,0032; 0,0594; 0,8078; 0,1296]
$x_D$ (Product)	[-]	0,6936	0,7453	0,8078
$x_B$	[-]	[0,2986; 0,1851; 0; 0,5163]	[0,2517; 0,1688; 0; 0,5795]	[0,1954; 0,1401; 0; 0,6645]
Catalyst	[-]	NKC-9	NKC-9	NKC-9
Catalyst amount	[kg]	25	25	25
Hole area	[-]	6%	6%	6%
Column Diameter	[m]	0,64	0,64	0,64
Column Height	[m]	19,4	19,4	19,4
$Q_c$	[kW]	1389,9	1055,8	716,2
$Q_r$	[kW]	1268,6	977,5	673,5

Table 13: MeOAc reactive-cyclic columns. Simulation results, higher duration of the VFP

	Unit of measure	Column 14, $t_{vap} = 150\text{ s}$	Column 15, $t_{vap} = 180\text{ s}$
Conversion	[-]	0,9153	0,9471
Rectifying Stags	[-]	5	5
Reactive Stages	[-]	17	17
Stripping Stages	[-]	4	4
Feed stage [from bottom]	[-]	[5; 22]	[5; 22]
$q$	[-]	1	1
$F$	[kmol/cycle]	[0,5; 0,5]	[0,5; 0,5]
$D$	[kmol/cycle]	0,495	0,495
$B$	[kmol/cycle]	0,505	0,505
$V \cdot t_{vap}$	[kmol/cycle]	1,1	1,1
$t_{vap}$	[s]	150	180
$t_{liq}$	[s]	0	0
$L$	[kmol/cycle]	0,9779	1,0295
$RR$	[-]	1,9755	2,0798
$BR$	[-]	2,1782	2,1782
$z_F$	[-]	[0; 1; 0; 0]	[0; 1; 0; 0]
	[-]	[1; 0; 0; 0]	[1; 0; 0; 0]
$x_D$	[-]	[0; 0,0357; 0,9243; 0,0400]	[0; 0,0255; 0,9568; 0,0177]
$x_D$ (MeOAc)	[-]	0,9243	0,9568
$x_B$	[-]	[0,0840; 0,0489; 0; 0,8671]	[0,0523; 0,0274; 0; 0,9203]
Catalyst	[-]	NKC-9	NKC-9
Catalyst amount	[kg]	25	25
Hole area	[-]	2%	2%
Column Diameter	[m]	0,78	0,78
Column Height	[m]	19,4	19,4
$Q_c$	[kW]	228,7	188,5
$Q_r$	[kW]	287,5	243,5

From the tables above (table 12, table 13) it is possible to notice two things: the first is that it is true that working with a lower duration of the vapour flow period is not a good choice when dealing with slow reactions (this is different for the fast ones, see Column 6 in 5.1.2); the second is that to work with higher  $t_{vap}$  it is necessary to change the trays configuration and hole area to prevent weeping. It was not possible to simulate columns with higher  $t_{vap}$  because it is not possible to go under a certain percentage of hole area in the trays, say 1%.

#### 4.2.2.2 $t_{liq}$ modification

To investigate further what happens in a reactive-cyclic column, the assumption of instantaneous LFP and so the hypothesis of no reaction during the liquid discharge was relaxed. To perform this modification, the algorithm used by Nielsen [30] to simulate the reactive-cyclic columns had to be a little modified to integrate the system of equations describing the reactive trays also during the LFP.

The duration of the LFP varies according to the type of trays assembled in the column: with Maleta trays [22], the discharge of the liquid happens simultaneously on each tray because of the presence of the sluice chamber so it is reasonable to say that a LFP of 10 seconds should be a reasonable estimate at this stage of the study; with the usual cyclic trays instead, as the discharge does not happen simultaneously on each tray but it is necessary to drain them starting from the bottom one to avoid backmixing, it is reasonable to assume 60 seconds of LFP for columns that have less than 30 trays. To further investigate this kind of feature, it was decided to also add an intermediate period of 30 seconds.

To avoid the above mentioned problems of weeping, the duration of the VFP has been chosen to be equal to 120 seconds.

In the following table it is possible to read the results of the simulation of the three resulting columns:

Table 14: MeOAc reactive-cyclic columns. Simulation results, nonzero LFP duration

	Unit of measure	Column 16, $t_{liq} = 10\text{ s}$	Column 17, $t_{liq} = 30\text{ s}$	Column 18, $t_{liq} = 60\text{ s}$
Conversion	[-]	0,8959	0,9158	0,9452
Rectifying Stags	[-]	5	5	5
Reactive Stages	[-]	17	17	17
Stripping Stages	[-]	4	4	4
Feed stage [from bottom]	[-]	[5; 22]	[5; 22]	[5; 22]
$q$	[-]	1	1	1
$F$	[kmol/cycle]	[0,5; 0,5]	[0,5; 0,5]	[0,5; 0,5]
$D$	[kmol/cycle]	0,495	0,495	0,495
$B$	[kmol/cycle]	0,505	0,505	0,505
$V*tvap$	[kmol/cycle]	1,1	1,1	1,1
$tvap$	[s]	120	120	120
$tliq$	[s]	10	30	60
$L$	[kmol/cycle]	0,9432	0,9692	1,011
$RR$	[-]	1,9055	1,9581	2,0423
$BR$	[-]	2,1783	2,1782	2,1782
$zF$	[-]	[0; 1; 0; 0]	[0; 1; 0; 0]	[0; 1; 0; 0]
	[-]	[1; 0; 0; 0]	[1; 0; 0; 0]	[1; 0; 0; 0]
$xD$	[-]	[0; 0,0383; 0,9047; 0,0570]	[0; 0,0353; 0,9248; 0,0399]	[0; 0,0264; 0,9548; 0,0188]
$xD$ (Product)		0,9047	0,9248	0,9548
$xB$	[-]	[0,1032; 0,0656; 0; 0,8312]	[0,0835; 0,0487; 0; 0,8678]	[0,0542; 0,0284; 0; 0,9174]
Catalyst	[-]	NKC-9	NKC-9	NKC-9
Catalyst amount	[kg]	25	25	25
Hole area	[-]	3%	3%	3%
Column Diameter	[m]	0,73	0,78	0,78
Column Height	[m]	19,4	19,4	19,4
$Qc$	[kW]	347,4	304,4	258,2
$Qr$	[kW]	328,2	287,6	243,3

The table above shows clearly that the conversion and the purity of the desired product get enhanced if the duration of the LFP is increased. It could be then a feasible option to work with a reduced  $t_{vap}$ , to reduce the possibility to reach weeping conditions, and increase a little the draining time of the LFP to reach the same conversion and desired purity of methyl acetate.

## 5. Cost analysis

In this chapter, a cost analysis will be performed on the columns that have been designed and simulated in the previous chapters.

### 5.1 Cost definitions

Before presenting the results of the cost analysis, it is important to describe what type of analysis it is and the steps adopted to perform it.

There are two types of costs that must be considered to perform a good cost analysis: the Capital Expenditures (CAPEX) that take into account all the costs of the equipment installed in a certain plant and the Operating Expenditures (OPEX) that comprehend the daily costs due to utilities, raw materials, etc.

In this work, the cost of the vessel of the column, the cost of the trays and the cost of the two heat exchangers (reboiler and condenser) will be considered as CAPEX; the cost of the steam and of the cooling water will be considered as OPEX.

While the operative expenditures are easier to estimate simply by multiplying the cost of the utility with the amount of the needed utility, for the capital expenditures it is necessary to spend some more words.

#### 5.1.1 CAPEX

Capital expenditures can be estimated thanks to cost indexes and Guthrie's formula. Knowing the past cost of a certain piece of equipment, it is possible to estimate the present one simply by multiplying that cost to the ratio between the present and the past cost index (the most famous cost index is the Marshall&Swift); furthermore, it is possible to evaluate the cost of a certain piece of equipment if it is known the cost of a similar piece with different dimensions, materials,

working conditions. Joining the two information together, it is possible to reach the following general formula:

$$Cost\ of\ B = Cost\ of\ A * \left(\frac{Cost\ index_B}{Cost\ index_A}\right) * \left(\frac{Dim_B}{Dim_A}\right)^\alpha * \left(\frac{Mat_B}{Mat_A}\right)^\beta * \left(\frac{Pre_B}{Pre_A}\right)^\gamma$$

The indexes used in this work can be found in the appendix alongside the complete equations used for each different piece of equipment.

## 5.2 Data and assumptions

From the simulation results, the following data must be retrieved to evaluate the CAPEX and the OPEX:

*Table 15: Useful data for the cost analysis*

<b>Column vessel</b>	
Pressure	Materials
Diameter	Height
<b>Column trays</b>	
Diameter	Total height
Tray spacing	Materials
Tray type	
<b>Heat exchangers</b>	
Exchange area	Materials
Pressure	Type of exchanger
<b>Utilities</b>	
Type of utility	Power exchanged

It is important also to point out some general assumptions used during the cost analysis:

- A year contains 8760 hours, but considering that a chemical plant needs maintenance, the amount of working hours has been reduced to 8000  $h/y$  to also consider the start-up and the shut-down (about one month of no production);
- For all the columns and the exchangers, it was possible to use carbon steel for the vessels and the trays; none of the reactants/products is corrosive, so the cheaper material was chosen;
- The type of trays varies according to the type of column: for the reactive columns, sieve trays were chosen (cheapest choice), while for the reactive cyclic columns, Maleta trays were used (the cost has been estimated to be about the double of the one of the sieve trays);
- For each column it was chosen to use a kettle-type reboiler and a fixed tubes-type condenser;
- The costs of the utilities were evaluated as the mean of the data taken from Intratec Solutions online database [39];
- To be able to confront the CAPEX [€] and the OPEX [€/y], the value of the capital expenditures had to be divided by the expected lifetime of the pieces of equipment. In this work, the expected lifetime of the columns and the exchangers was set to 10 years, using a very conservative approach;
- Cooling water enters the two different case studies with two slightly different temperatures: for the MTBE synthesis, cooling water is sent to the condenser at a temperature of 16°C; for the MeOAc synthesis, cooling water is sent to the condenser at a temperature of 18°C. The difference is due to the fact that the distillate product of the MTBE has a boiling point of about 25°C at the operating pressure.



### 5.3 Case study 1: MTBE synthesis

In this paragraph, the results of the cost analysis of the 6 columns regarding the synthesis of MTBE will be presented. The columns refer to the ones simulated in the paragraphs 4.1.1 and 4.1.2.

Table 16: Cost analysis results for the reactive MTBE columns

	Unit of measures	Column 1	Column 2	Column 3
Vessels - A	[€]	47.435,85 €	51.843,12 €	54.408,03 €
Trays - B	[€]	4.133,77 €	2.858,63 €	2.112,93 €
Column cost - A+B	[€]	51.569,62 €	54.701,76 €	56.520,95 €
Condenser - C	[€]	85.645,09 €	85.645,09 €	85.645,09 €
Reboiler - D	[€]	10.754,77 €	10.754,77 €	10.754,77 €
Exchangers cost - C+D	[€]	96.399,86 €	96.399,86 €	96.399,86 €
CAPEX - A+B+C+D	[€]	147.969,48 €	151.101,62 €	152.920,81 €
Cost of cooling water - E	[€/y]	11.441,16 €	11.441,16 €	11.441,16 €
Cost of steam - F	[€/y]	20.265,79 €	20.265,79 €	20.265,79 €
OPEX - E+F	[€/y]	31.706,95 €	31.706,95 €	31.706,95 €
Total annualized costs	[€/y]	46.503,89 €	46.817,11 €	49.999,03 €

Table 16 shows the results of the cost analysis performed on the three reactive columns producing MTBE. The results of the simulations are reported in the table 4 alongside some of the specifications; the three columns differ just for the tray spacing.

It is clear that for the reactive case, there are no noteworthy differences. Even if Column 3 is the most expensive, as the differences are really small, it will be the reference case for the reactive

MTBE columns: the tray spacing is the most similar to the one of the Maleta trays for the reactive-cyclic cases reported in table 17.

Table 17: Cost analysis results for the reactive-cyclic MTBE columns

	Unit of measures	Column 4	Column 5	Column 6
Vessels - A	[€]	19.838,12 €	16.744,04 €	17.743,93 €
Trays - B	[€]	1.158,75 €	905,56 €	973,47 €
Column cost - A+B	[€]	20.996,88 €	17.649,60 €	18.717,41 €
Condenser - C	[€]	96.736,07 €	87.382,30 €	391.183,54 €
Reboiler - D	[€]	17.872,31 €	15.085,94 €	67.390,07 €
Exchangers cost - C+D	[€]	114.608,38 €	102.468,23 €	458.573,61 €
CAPEX - A+B+C+D	[€]	135.605,26 €	120.117,83 €	477.291,02 €
Cost of cooling water - E	[€/y]	20.989,43 €	18.019,50 €	180.130,55 €
Cost of steam - F	[€/y]	44.257,41 €	34.107,11 €	341.071,07 €
OPEX - E+F	[€/y]	65.246,84 €	52.126,61 €	521.201,63 €
Total annualized costs	[€/y]	78.807,37 €	64.138,40 €	568.930,73 €

Table 17 shows the results of the cost analysis performed on the three reactive-cyclic columns producing MTBE. The specifications and the results of the simulations can be found in table 7.

As stated already in chapter 4, column 6 is not physically buildable because the duration of the VFP would be too short and the vapour could not reach the top of the column; furthermore, the condenser and the reboiler would require really large exchange areas resulting in unfeasible costs for the resulting scheme.

The two other columns (4 and 5) are instead worthy of discussion: the results show clearly that the driving force approach (column 5) is capable of reducing the costs of the utilities and

consequently also of the exchangers (because the amount of power that has to be exchanged is smaller). Column 5 appears to be better because it is cheaper both in terms of CAPEX and in terms of OPEX. What is important to underline is that the process is surely intensified only at a local scale: as the feed must be inserted with a value of  $q$  different from 1, to reach the maximum driving force it could be necessary to preheat it thus losing, from a global point of view, that heat that the column is capable to save.

## 5.4 Case study 2: MeOAc synthesis

In this paragraph, the results of the cost analysis of the columns regarding the synthesis of MeOAc will be presented. It was decided to analyse only the columns that reach a purity of MeOAc greater than 0,9 alongside the base case already studied by Nielsen and the only reactive columns.

Table 18: Cost analysis results for the reactive MeOAc columns

	Unit of measures	Column 8	Column 9
Vessels - A	[€]	71.247,98 €	82.637,41 €
Trays - B	[€]	4.418,56 €	3.770,26 €
Column cost - A+B	[€]	75.666,53 €	86.407,68 €
Condenser - C	[€]	46.482,60 €	46.482,60 €
Reboiler - D	[€]	17.237,04 €	17.237,04 €
Exchangers cost - C+D	[€]	63.719,64 €	63.719,64 €
CAPEX - A+B+C+D	[€]	139.386,18 €	150.127,32 €
Cost of cooling water	[€/y]	2.673,26 €	2.673,26 €
Cost of steam	[€/y]	41.872,18 €	41.872,18 €
OPEX	[€/y]	44.545,43 €	44.545,43 €
Total annualized costs	[€/y]	58.484,05 €	59.558,17 €

Table 18 collects the results of the cost analysis performed on the reactive towers simulated in the paragraph 4.2.1; Column 7 was not reported because after the dimensioning, there were no optimal diameters to prevent both weeping and flooding. Also in this case, there are no noteworthy differences in the total annualized costs because the only difference between the two columns lies in the distance between the trays: it is true that a column with a smaller tray spacing is more subject to flooding, but it is also true that the highest the space between trays, the highest the column height.

Table 19: Cost analysis results for the reactive-cyclic MeOAc columns; base case and  $t_{vap}$  modification

	Unit of measures	Column 10	Column 14	Column 15
Vessels - A	[€]	84.515,70 €	97.826,32 €	97.826,32 €
Trays - B	[€]	8.228,09 €	10.177,87 €	10.177,87 €
Column cost - A+B	[€]	92.743,79 €	108.004,20 €	108.004,20 €
Condenser - C	[€]	51.294,28 €	37.986,11 €	33.326,63 €
Reboiler - D	[€]	31.626,07 €	26.693,02 €	23.961,14 €
Exchangers cost - C+D	[€]	82.920,35 €	64.679,13 €	57.287,77 €
CAPEX - A+B+C+D	[€]	175.664,14 €	172.683,33 €	165.291,96 €
Cost of cooling water	[€/y]	3.705,16 €	2.329,19 €	1.919,65 €
Cost of steam	[€/y]	106.499,83 €	82.038,13 €	69.485,18 €
OPEX	[€/y]	110.204,99 €	84.367,31 €	71.404,83 €
Total annualized costs	[€/y]	127.771,40 €	101.635,65 €	87.934,03 €

Table 19 contains the results of the cost analysis performed on the base case column and on the columns with higher  $t_{vap}$  simulated in the paragraph 4.2.2 and 4.2.2.1 respectively. Column 10 refers to the base case with  $t_{vap} = 120$  seconds, while columns 14 and 15 refer respectively to the

towers working with 150 and 180 seconds of duration of the vapour flow period. In this case the trend of the total annualized costs shows that increasing  $t_{vap}$  the costs decrease; the reason behind this behaviour lies in the fact that each cycle becomes longer so in a year there is a lower amount of cycles and so it is lower also the amount of heat and steam (the biggest contribute to the TAC is clearly given by the cost of the hot utility) that must be provided to the reboiler. Following this trend, it should be a reasonable choice to work with the highest possible  $t_{vap}$  but it is important to remember that increasing too much the duration of the vapour flow period is unfeasible because the flow of the vapour in the column becomes slower and then weeping phenomena could occur; this could be avoided by reducing the number of holes in the trays, but it is clearly not possible to remove them all.

Table 20: Cost analysis results for the reactive-cyclic MeOAc columns;  $t_{liq}$  modification

	Unit of measures	Column 16	Column 17	Column 18
Vessels - A	[€]	91.155,96 €	97.826,32 €	97.826,32 €
Trays - B	[€]	9.184,61 €	10.177,87 €	10.177,87 €
Column cost - A+B	[€]	100.340,57 €	108.004,20 €	108.004,20 €
Condenser - C	[€]	49.800,06 €	45.735,52 €	40.915,18 €
Reboiler - D	[€]	29.091,98 €	26.699,06 €	23.948,35 €
Exchangers cost - C+D	[€]	78.892,03 €	72.434,57 €	64.863,52 €
CAPEX - A+B+C+D	[€]	179.232,60 €	180.438,77 €	172.867,72 €
Cost of cooling water	[€/y]	3.537,47 €	3.100,21 €	2.629,40 €
Cost of steam	[€/y]	93.650,91 €	82.072,95 €	69.432,95 €
OPEX	[€/y]	97.188,38 €	85.173,15 €	72.062,35 €
Total annualized costs	[€/y]	115.111,64 €	103.217,03 €	89.349,12 €

Table 20 is the sum up of the results of the cost analysis performed on the columns simulated in the paragraph 4.2.2.2. These columns are linked by the fact that they have the same duration of the vapour flow period (120 s) but different durations of the liquid flow period. Until now all the columns have been studied considering as instantaneous the discharge of the trays due to the LFP and only now this hypothesis has been relaxed. The columns show a trend that is similar to the ones of table 19, the higher the time, the lower the costs and the reason behind this behaviour is the same discussed above but looking also at table 13 and 14, it is possible to increase the duration of a cycle without reducing too much the velocity of the vapour that rises in the column during the VFP (the fraction of hole area is slightly higher in Table 14).

## 6. Discussion and conclusions

This thesis work has been conducted to investigate whether the cyclic feature can be a valid option to make the reactive columns work better. To do so, several columns have been designed, simulated and then analysed in terms of costs, purity of the products and energy consumption. What emerges from the results will be briefly commented below to make a summary of everything that has been done.

The study conducted on the MTBE case shows that including the cyclic feature when dealing with a very fast reaction could be a viable option to reduce drastically the number of stages and so the dimensions of the column. There are no significant differences in terms of purity of the products and it is important to remember that the columns have been designed to have all the same productivity. What emerges from Table 4 and 7 is that the number of trays and so the total height of the column are considerably reduced. In numbers, the reactive column needs 30 trays while the reactive cyclic can do the same job using only 6 trays. The direct consequence of this result is the fact that also the capital expenditures are reduced in the same way, especially the ones of the column alone. Looking at Table 16 and 17 and focusing the attention on Column 3 (reactive) and 4 (reactive-cyclic), the CAPEX of the column are reduced of more than 64%. What makes the reactive columns still a better solution to implement is the fact that according to these results, more energy should be consumed to make the reactive-cyclic columns work and, in the long term, also more money because just after one year and a half, the total costs of the reactive-cyclic column become higher than the total costs of the pure reactive tower.

The same kind of conclusions can be taken also for the case of the Methyl Acetate synthesis. The cyclic feature is a good way to reduce the number of trays and so the total height of the columns, but in this case the capital expenditures do not decrease because the diameter of the columns gets bigger so the CAPEX remains quite similar between the reactive and the reactive-cyclic cases. Also for the slow reactions, it seems that the cyclic feature does not give proper improvements to the process; even though the purity remains the same and the productivity can be modulated

to be the same of a reactive tower, the columns without the cyclic feature seem to be less energy consuming and also cheaper.

An important result obtained during this thesis work is the relaxation of the hypothesis of instantaneous LFP. It is important to investigate further if the reaction continues also during the LFP because even though the most part of the reaction happens during the vapour flow period thanks to the mixing given by the vapour rising in the column and because the continuous removal of the products pushes furtherly the equilibrium towards the right hand side of the reaction, those seconds of liquid flow period can push even furtherly the conversion. This kind of behaviour must be taken into account when designing the columns above all if the available trays are the one studied by Toftegård et al. [23] and the column is quite high: if the trays must be drained one by one starting from the bottom to avoid back mixing, the resulting LFP in a column with approximately 15-20 trays and a draining period of 2-3 seconds starts to be a non negligible amount of time (i.e. 30-60 seconds). Further studies could be done to put also this feature in a more complete design method.

According to this work of thesis, it seems that the cyclic feature does not give the expected results when added to a reactive column, but it is important to stress out that new studies should be done to investigate further what would happen with different types of reactions. It could be interesting to make a more general study about what is and what is not a fast reaction suitable for reactive distillation and to apply then the cyclic feature on a general model of slow reaction to see when and how the addition of this feature could bring improvement in the process.



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# Appendix

The following chapter contains all the numerical data and the numerical correlations used in this thesis work alongside the MATLAB code used to design the columns and to simulate the reactive-cyclic ones.

## A. Thermodynamic properties

### Heat of vaporization

The heat of vaporization has been calculated thanks to the following correlation and data:

$$\Delta H^{vap} = C_1 * (1 - T_r)^{C_2 + C_3 * T_r + C_4 * T_r^2} \left[ \frac{kJ}{kmol} \right]$$

$$T_r = \frac{T}{T_c}$$

Table 21: Heat of vaporization parameters

	$C_1$	$C_2$	$C_3$	$C_4$	$T_c [K]$	Range of validity [K]	Source
Acetic acid	40179	2,6037	-5,0031	2,7069	591,95	289,81 < T < 591,95	Perry
Isobutene	32720	0,383	0	0	417,9	132,81 < T < 417,9	Perry
Methanol	52390	0,3682	0	0	512,64	175,47 < T < 512,64	Perry
Methyl Acetate	44920	0,3685	0	0	506,55	175,15 < T < 506,55	Perry
MTBE	42024	0,37826	0	0	497,1	164,55 < T < 497,1	Perry
Water	52053	0,3199	-0,212	0,25795	647,13	273,17 < T < 647,13	Perry

## Vapour pressure

The vapour pressure has been calculated thanks to the extended version of the Antoine correlation and the data reported in the table 22:

$$P_{sat}(T) = \exp\left(C_1 + \frac{C_2}{T} + C_3 * \ln(T) + C_4 * T^{C_5}\right) \quad [Pa]$$

Table 22: Vapour pressure parameters for extended Antoine equation

	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$	Range of validity [K]	Source
Acetic acid	53,27	-6304,5	-4,2985	$8,8865 * 10^{-18}$	6	289,81 < T < 591,95	Perry
Isobutene	102,5	-5021,8	-13,88	0,020296	1	132,81 < T < 417,9	Perry
Methanol	81,768	-6876	-8,7078	$7,1926 * 10^{-6}$	2	175,47 < T < 512,64	Perry
Methyl Acetate	61,267	-5618,6	-5,6473	$2,108 * 10^{-17}$	6	175,15 < T < 506,55	Perry
MTBE	55,875	-5131,6	-4,9604	$1,9123 * 10^{-17}$	6	164,55 < T < 497,1	Perry
Water	73,649	-7258,2	-7,3037	$4,1653 * 10^{-6}$	2	273,17 < T < 647,13	Perry

## Activity Coefficient models

In this work, two different activity coefficient models have been used for the MTBE case and the MeOAc case. They will be briefly summarized in the following paragraphs.

### NRTL

The equation used to evaluate the activity coefficient for NRTL model, is the following [26]:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{NC} \tau_{j,i} * G_{j,i} * x_j}{\sum_{k=1}^{NC} G_{k,i} * x_k} + \sum_{j=1}^{NC} \left[ \frac{x_j * G_{i,j}}{\sum_{k=1}^{NC} G_{k,j} * x_k} * \left( \tau_{i,j} - \frac{\sum_{k=1}^{NC} \tau_{k,j} * G_{k,j} * x_k}{\sum_{k=1}^{NC} G_{k,j} * x_k} \right) \right]$$

where  $\tau_{i,j}$  and  $G_{i,j}$  are defined as follows:

$$\tau_{i,j} = \frac{A_{i,j}}{T} \quad , \quad G_{i,j} = \exp(\alpha_{i,j} * \tau_{i,j})$$

The model parameters are collected in the following table:

Table 23: NRTL parameters  $A_{i,j}$  and  $\alpha_{i,j}$  for MeOAc system. A: Acetic acid, B: Methanol, C: Methyl Acetate, D: Water [37]

$A_{i,j} [K]$	A	B	C	D	$\alpha_{i,j} [-]$	A	B	C	D
A	0	342,0151	-239,2462	-48,5157	A	0	0,30	0,30	0,30
B	-310,2822	0	130,5047	-57,8859	B	0,30	0	0,30	0,30
C	415,2702	234,8660	0	269,5857	C	0,30	0,30	0	0,35
D	385,2682	292,9637	866,2183	0	D	0,30	0,30	0,35	0

## Wilson

The equation used to evaluate the activity coefficient for Wilson model, is the following [26]:

$$\ln(\gamma_i) = 1 - \ln\left(\sum_{j=1}^{NC} x_j * \Lambda_{i,j}\right) - \sum_{k=1}^{NC} \left(\frac{x_k * \Lambda_{k,i}}{\sum_{j=1}^{NC} x_j * \Lambda_{k,j}}\right)$$

where  $\Lambda_{i,j}$  is evaluated with the following expression

$$\Lambda_{i,j} = \frac{V_{m,i}}{V_{m,j}} * \exp\left(-\frac{a_{i,j}}{T}\right)$$

and the model parameters are taken from table 24.

Table 24: Wilson parameters  $a_{i,j}$  and  $V_{m,i}$  for MTBE system. A: Isobutene, B: Methanol, C: MTBE [18]

$a_{i,j} [K]$	A	B	C	$V_{m,i} [m^3/kmol]$
A	0	49,4802	8,87958	A 93,33
B	1243,186	0	711,7	B 44,44
C	-0,01494	-197,9	0	C 118,8

## B. Dimensioning correlations

The columns studied in this work have been dimensioned using the correlations presented below. While for the reactive distillation it was possible to use Fair correlation to evaluate the entrainment flood prediction, there is still no correlation for Maleta trays that is capable of evaluating the flooding conditions. That is why the pure Reactive Columns have been dimensioned to avoid both the flooding and the weeping conditions, while the Reactive-Cyclic ones have been dimensioned taking into account only the weeping correlation.

### Flooding Correlations

$$\left(\frac{L}{G}\right)_i = \frac{L_i}{V_i} * \sqrt{\frac{\rho_{V,i}}{\rho_{L,i}}}$$

$$C_{bs,i} = 0.0105 + 8.127 * 10^{-4} * TS^{0.755} * \exp\left(-1.463 * \left(\frac{L}{G}\right)_i^{0.842}\right)$$

$$v_{flood,i} = C_{bs,i} * \left(\frac{\sigma_i}{20}\right)^{0.2} * \sqrt{\frac{\rho_{L,i} - \rho_{V,i}}{\rho_{V,i}}}$$

The flooding correlations have been used for each tray of the reactive columns gaining the data from the Aspen Hysys simulations (density of both the phases, mass flow of both the phases, surface tension) and choosing a certain Tray Spacing. Scaling the flooding velocity with a security factor, it was then possible to evaluate the bubble area, the total area and the diameter. The hypothesized diameter is then approximated and used to check if the real velocity remains under the flooding one for each tray.

## Weeping Correlations

After gaining a hypothesized diameter ( $d_c$ ) with the flooding correlations, it is necessary to check if it is feasible to use it also to prevent the weeping. Before starting the weeping check, it is important to gain the data (molar hold-up, temperature, molar vapour flows, vapour density) from the simulations of the columns performed in Aspen Hysys or MATLAB, estimate the liquid volume on each tray, assign hole diameter ( $d_h$ ) and calculate the liquid height on each tray ( $h_k$ ). Then it is possible to use

$$K_i = 33.9025 + \left( \frac{-1.4285 * 10^5 - 33.9025}{1 + \left( \frac{h_i}{1.18 * 10^{-9}} \right)^{0.4295}} \right)$$

$$v_{weep,i} = \frac{K_i - 0.9 * (25.4 - d_h)}{\sqrt{\rho_{i-1}^v}}$$

to estimate the weeping velocity and to check then if it is always smaller than the real velocity of the vapour flowing on each tray.



## C. Cost analysis data and correlations

### Columns vessels

The costs of the vessels of the columns have been estimated with the following correlations and parameters [40]:

$$C_{vessel} = \frac{1110}{280} * 101.9 * D^{1.066} * H^{0.802} * (2.18 + F_c)$$

with D and H in ft and  $F_c = F_m * F_p$ .

$P$ [psia]	≤ 50	100	200	300	400	500	600	700	800
$F_p$	1.00	1.05	1.15	1.20	1.35	1.45	1.6	1.8	1.9
<i>Material</i>	<i>Carbon Steel</i>	<i>Stainless Steel</i>	<i>Monel</i>	<i>Titanium</i>					
$F_m$	1.00	3.67	6.34	7.89					

### Columns trays

The costs of the columns trays have been estimated with the following correlations and parameters [40]:

$$C_{trays} = \frac{1110}{280} * 4.7 * D^{1.55} * H_{TOT} * F_c$$

with D and  $H_{TOT}$  in ft.

$$H_{TOT} = (N_{trays} - 1) * TS + H_{Top-Bottom}$$

$$H_{Top-Bottom} = 5 m$$

$$F_c = F_s + F_t + F_m$$

Tray Spacing [in]	24	18	12	
$F_s$	1.00	1.4	2.2	
Tray type	No downcomer	Sieve	Valve	Bubble cap
$F_t$	0.0	0.0	0.4	1.8
Tray Material	Carbon Steel	Stainless Steel	Monel	
$F_m$	0.0	1.7	8.9	

## Heat exchangers

The costs of the heat exchangers have been estimated with the following correlations and parameters [40]:

$$C_{exch} = \frac{1110}{280} * 101.3 * A^{0.65} * (2.29 + F_c)$$

with A in ft<sup>2</sup>.

$$F_c = (F_d + F_p) * F_m$$

Material Shell/Tube	CS/CS	Pressure [psi]	≤ 150	Type	Kettle
$F_m$	1	$F_p$	0	$F_d$	1.35

For the estimation of the heat exchange area,

$$Q = U * A * \Delta T_{ml}$$

Considering for the condenser a global coefficient  $U_c$  equal to 580 W/m<sup>2</sup>K and for the reboiler

$$U_r \Delta T_{ml,r} = 11250 \frac{Btu}{h \text{ ft}^2}$$