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**OPTIMAL DESIGN AND FLEXIBILITY
ASSESSMENT OF INTENSIFIED
SOLUTIONS FOR BIOREFINERY
DOWNSTREAM PROCESSING: THE DWC
CASE STUDY**

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*Success is not final; failure is not fatal:
It is the courage to continue that counts.*

Winston Churchill

Preface

This thesis has been made possible thanks to the SUPER (Sustainable Process Engineering Research) team lead by Prof. Flavio Manenti of Department of Chemical, Material, and Chemical Engineering of Politecnico di Milano.



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List of Abbreviations

ABE	Acetone-Butanol-Ethanol
ABE/W	Acetone-Butanol-Ethanol-Water
CAPEX	CAPital EXpenditure
CEPCI	Chemical Engineering Plant Cost Index
DCM	Distillation Curve Map
DF	Dynamic Flexibility Index
DOF	Degrees of freedom
DWC	Divided Wall Column
D/F	Distillate/Feed flowrate ratio
EI99	Eco Indicator 99
FUGK	Fenske-Underwood-Gilliland-Kirkbride
GHG	Green House Gas
HETP	Height equivalent to the theoretical plate
HFO	Heavy Fuel Oil
LCA	Life Cycle Assessment
MATLAB	MATrix LABoratory
M&S	Marshall and Swift

NC	Number of Components
NG	Natural Gas
NHV	Net Heating Value
NS	Number of Stages
NRTL	Non-Random Two Liquids
ON	Octane number
OPEX	Operating Expenditure
RCM _s	Residue Curve Maps
RI	Resilience Index
SF	Stochastic Flexibility Index
TAC	Total Annualized Cost
TNB	Normal Boiling Temperature
VLE	Vapor-Liquid equilibrium
V/F	Vapor/Feed Flowrate ratio

Abstract

This M.Sc. thesis work deals with the steady-state simulation of Acetone-Ethanol-Butanol (ABE) process downstream separation plant through the Divided Wall Column (DWC).

This study is carried out in collaboration with the SUPER (Sustainable Process Engineering Research) group of Department of Chemistry, Material, and Chemical Engineering “Giulio Natta” of Politecnico of Milan, to continue the work of Ing. A. Di Pretoro in his publication “Flexibility Assessment of a Biorefinery Distillation Train: Optimal Design under Uncertain Conditions”.

Until the first half of the 20th century, the ABE fermentation to obtain biobutanol is the most spread industrial-scale fermentation process, then with the rising of oil and petrol, the alcoholic fermentation was progressively abandoned due to its low competitiveness. In the last 20 years, there has been an increasing interest in the production of energy from renewable sources, because of the growth of global warming and climate change, the increase of oil price and the existing legislation restricting the use of non-renewable energy sources.

The use of DWC instead of the classic fermentation process, or train of columns, studied in the aforementioned article, allows obtaining butanol from ABE mixture with only one unit operation.

In this thesis, there are two principal different parts. The first concern the optimization, in terms of cost and emission of CO₂, of the case study in nominal condition. In the second part, flexibility assessment and optimization, varying the feed, are studied.

Finally, for both parts, a comparison with the indirect train of columns is doing to test which configuration is the most convenient in terms of cost, emission, and flexibility.

Sommario

La presente tesi si occupa della simulazione in stazionario di un impianto di separazione a valle del processo Acetone-Butanolo-Etanololo (ABE) attraverso l'utilizzo di una Divided Wall Column (DWC).

Questo studio è in collaborazione con il gruppo SUPER (SUustainable Process Engineering Research) del dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta" del Politecnico di Milano, per continuare il lavoro dell'ingegner Di Pretoro nell'articolo "Flexibility Assessment of a Biorefinery Distillation Train: Optimal Design under Uncertain Conditions"

Fino alla prima metà del 20mo secolo, la fermentazione dell'ABE al fine di ottenere biobutanolo era il processo di fermentazione più diffuso in scala industriale, con il sorgere del petrolio e delle benzine, la fermentazione alcolica è stata progressivamente abbandonata a causa della sua bassa competitività. Negli ultimi vent'anni, l'interesse nella produzione di energia da risorse rinnovabili è rinato a causa dell'aumento del riscaldamento globale e del cambiamento climatico, al prezzo del petrolio sempre in aumento e alla presenza di leggi che limitano l'utilizzo di energia da fonti non rinnovabili.

La DWC in sostituzione del classico processo di fermentazione, o del treno di colonne, analizzato nell'articolo precedentemente citato, permette di ottenere biobutanolo dalla miscela ABE, con un'unica unità operativa.

Questa tesi si compone di due parti principali. La prima ha lo scopo di ottimizzare, in termini di costi e emissioni di CO₂, il case-study in condizioni nominali. Nella seconda parte è stata fatta una valutazione della flessibilità variando il feed, con conseguente ottimizzazione.

Infine, entrambe le analisi sono state confrontate con il treno indiretto di colonne, per analizzare quale configurazione sia più conveniente da un punto di vista economico, di flessibilità ed emissioni.

CHAPTER 1

INTRODUCTION

This thesis work aims to study the biorefinery downstream processing for biobutanol production from acetone-butanol-ethanol-water (ABE/W) mixture. In this first chapter the most important theoretical fundamentals for this work will be covered: in the first paragraph 1.1, the story, utilization, and state of the art of the separation of ABE/W mixture will be explained. Then there is an important introduction on a divided wall column, the case study of this research and an innovative way for ABE/W separation. Finally, the important concept of flexibility analysis will be treated. Flexibility analysis is deepened in a later chapter to study the behaviour of the column under uncertain conditions.

1.1 History of Acetone-Butanol-Ethanol

Due to the high cost and extensive oil consumption, the study of biofuels over fossil fuels became more important in the last decades. Among biofuels, bio-based butanol is expected to have an important role in the next years [1]. Butanol is a superior biofuel and it can be produced from different cellulosic biomass. In general, Biofuels are more environmentally benign compared to hydrogen, natural gas, and syngas. Moreover, butanol is preferred to ethanol thanks to its higher energy density, lower volatility, and lower hygroscopicity, all these properties make butanol more gasoline-like. It can also be used for further processing of advanced biofuels such as butyl levulinate [2]. The most typical way to produce bio-butanol is the fermentation of acetone-butanol-ethanol. The Acetone Butanol Ethanol (ABE)fermentation has an interesting history that starts from Louis Pasteur in 1861 when he discovered that butanol can be produced from bacteria. Then in 1912 Chain Weizmann observed that *Clostridium acetobutylicum* can produce alcohols metabolizing cereal and potatoes. Although butanol is a superior biofuel during World War I, England became interested in acetone

to produce explosives. In 1918 Commercial Solvents Corporation built the first ABE fermentation plants in Indiana, to produce butyl acetate and a primary component of paint lacquers. After 1936, ABE plants were built throughout the United States and the process became second only to yeast-based ethanol fermentation. During the second half of the XX century, bio-butanol production decreased, due to the presence of cheapest and more available fuel, as fossil carbon feedstock. This led to stop many plants, after 1960 the only ones working were in South Africa, until 1980, Russia, until 1990, and China, until 2004. The history of ABE plants in China starts in the 1950s, peaked in the 1980s and as said before at the end of the century with the severe expansion of the petrochemical industry [1]. ABE fermentation returns of interest in 1970 with the rising cost of petrochemical feedstocks and the energy crisis. Thanks to these new studies for the solventogenic clostridia there was a development of strains that improved the fermentation characteristic [3]. During the last years, there is a huge interest in the production of renewable resources, the reason is the problem of global warming and climatic change. In recent years the largest growth is recorded in China, where the annual production of bio-butanol amounted to 210,000 tons in 2008 and is expected to reach 1 Million Ton in the next few years [1]. In ABE fermentation usually less than 2% (w/v) can be obtained from the fermentation broth but the ethanol yeast is almost 12-15%(w/v). To obtain butanol from the broth, intensive energy is required. This is one of the main problems of the biobutanol production, with the price of the feedstock [4]. The present aim is to make bio-butanol competitive, but there are several challenges to overcome:

- Expensive feedstock and substrate
- Strong product inhibition by butanol and acetone
- Low productivity and ABE yield in batch fermentation.

To solve the problem of expensive feedstock efforts are being to use agriculture residues and energy crops as a reagent to produce butanol with

the same microorganisms. To avoid product inhibition hyper-butanol-producing strains are being developed, such as *C.beijerinckii* BA101 [5]. In the past, the more important solventogenic clostridial species for the production of butanol were *C.acetobutylicum* ATCC 824 and *C.beijerinckii* NCIMB 8052. The latter has a greater potential in the industrial plants due to a broader substrate range and an optimum pH value for this type of production. From the study of *C.beijerinckii* NCIMB 8052, the most promising *C.beijerinckii* BA101 was discovered using chemical mutagenesis. Through the use of pilots, plants were confirmed that it is easy to handle in a simple, cheaper to use in industrial scale and more stable compared to strain degeneration [3]. As far as concern the substrate before the 1950s, the primary substrate used in this fermentation was corn and molasses, the latter is easy handily and offers a better utilization by saccharolytic clostridia. Instead of corn Ezeji et al [3]. tested liquefied corn meal and corn steep liquor showing that these substrates have a great potential in bioconversion to acetone-butanol, on the other end a problem for the long-term fermentation is the presence of sodium metabisulfite. Recently, to lower costs of production the investigation of the new substrate has become important. Renewable and economically feasible substrates ,such as agricultural wastes, are considered and the most promising is considered Lignocellulose, that is also the most abundant renewable resource [cf. Table 1.1]. Finally, with the study of genetic engineering of butanol producing strains the product inhibition became lower and simultaneously productivity and butanol yield became higher [6]. Another important challenge in the ABE fermentation study is the design of the reactor, in particular, it is possible to compare Batch, Fed-Batch and Continuous fermenters. About that Groot et al. compared batch fermenters and the continuous one and these studied assessed that the second has better productivity [7]. The Batch process is considered the most simple and common method for this fermentation but using this method the production is low due to the downtime, long lag phase, and product inhibition.

The first two problems can be eliminated with continuous or Fed-batch techniques.

Fermentation Parameters	Glucose	Cornstarch	Maltodextrins	Soy molasses	Agricultural wastes	Packaging peanuts
Acetone [g/L]	4.3	7.7	6.8	4.2	4.8	5.7
Butanol [g/L]	19.6	15.8	18.6	18.3	9.8	15.7
Ethanol [g/L]	0.3	1.2	0.3	0.3	0.2	0.3
Total ABE [g/L]	24.2	24.7	22.8	22.8	14.8	21.7
ABE productivity [g/L/h]	0.34	0.34	0.37	0.19	0.22	0.20
ABE yield [g/g]	0.42	0.44	0.50	0.39	N.C.	0.37

Table 1. 1-Production of butanol, acetone and ethanol from different substrates using *C.beijerinckii* [3]

To increase the productivity, it is possible to increase the concentration of cells in bioreactors or to fix cells onto gel particles or supports. Fed-Batch fermentation is an industrial technique, it is useful when high substrate concentration is toxic to the culture, but since butanol is toxic for *C. acetobutylicum*, this method can be used only with some product recovery technique such as gas stripping or pervaporation [cf. Table 1.2]. In recent years, the most important improvements in ABE fermentation design are linked to the downstream processes [8] studying the difference between the single unit or single-step operation and multi-stage integrated processes (cf. Table 1.1 and Table 1.2). Compared with conventional processes the integrated ones can improve product yield and productivity. In the next tables, the most promising techniques are evaluated: adsorption, pervaporation, liquid-liquid extraction, and gas stripping. The particularity of these integrated processes is that butanol can be removed during the fermentation from the broth, and this allows obtaining a bigger concentration maintaining the level of toxicity under the limits.

Fermentation process	Product removal technique	ABE [g]	Glucose [g]	Yield [g/g]	Prod. [g/L/h]
Batch [control]	None	24.2	59.8	0.42	0.34
Batch	Gas stripping	75.9	161.7	0.47	0.60
Fed-Batch	Gas Stripping	233	500	0.47	1.16
Continuos	Gas stripping	460	1163	0.40	0.91
Batch	Pervaporation	32.8	78.2	0.42	0.50
Fed-Batch	Pervaporation	165.1	384	0.43	0.98

Table 1. 2-Production of ABE in integrated fermentation product removal system [3]

Adsorption is considered the most energy-efficient process from butanol recovery, the adsorption consists of a packed column with an adsorbent material (carbon, zeolite, or polymeric resins) on which butanol is adsorbed. On the other hand, this method has some problems to resolve: not all promising adsorbents have been studied in situ with butanol fermentation, the adsorption of acetone and ethanol can inhibit the adsorption of butanol, the recovery rate is difficult to find in works of literature and during the adsorption of nutrients there could lower their efficiency. Pervaporation is a membrane-based process, this method consists of a selective membrane used to remove solvent from the fermentation broth [3]. Quereshi and Blaschek [8] applied this technique to recover butanol from broth and with a batch reactor, the productivity remains constant but in a fed-batch reactor it increases from 0.35 to 0.98 g/L/h thanks to the reduction in product inhibition. About gas stripping, it has many advantages in butanol recovery such as operational simplicity and low cost for equipment investment and, for these reasons, it has been considered one of the most important methods for butanol recovery. Table 1.3 shows that with gas stripping the productivity increases.

Strategy	Production of ABE [g/L/h]	Yield of ABE [g/g]	Titer of ABE [g/L]	Ferment mode ^c
Pervaporation	0.18	0.31-0.35	155	F
	0.14	0.34	42	F
	1.72	0.28	13.1	C
	0.98	0.43	165.1	F
	0.30	0.35	57-195	C
Liquid-Liquid extraction	0.14	0.35	23.8	F
	-	0.40	29.8	B
	-	0.38	27.9	B
	-	-	29.9	B
	2.5	0.35	25.3	C
	10.9	0.38	20.3	C
Gas stripping	0.26	0.38	69.1	F
	0.41	0.32	108.5	F
	1.16	0.47	232.8	F
	0.59	0.36	81.3	F
	0.53	0.36	172.1	F
Vacuum	0.34	0.26	45.9	B
Perstraction	0.21	0.44	136.6	B
	0.24	0.37	57,8	F
Adsorption	0.92	0.32	23.2	B
	1.33	0.32	59.8	F
	0.92	0.32	29.8	B
	0.30	0.20	31.6	F

^c, B=batch, F=fed-batch, C= continuous

Table 1. 3 -Integrated inhibitory product recovery strategies for enhanced ABE fermentation [9]

On the other hand, this technique consumes a bigger quantity of energy [7] if compared to others. Regarding the liquid-liquid extraction, it has the lowest energy consumption but nowadays it can be used only in lab-scale ABE fermentation.

Strategy	Advantages	Disadvantages	Selectivity	Energy requirements (Mj/kg)
Pervaporation	High selectivity	Fouling problem, membrane material cost	2-209	2-145
Liquid-liquid extraction	High selectivity	Emulsion, extraction cost, toxic to the culture	1.2-4100	7.7
Gas stripping	No fouling, easy to operate, no harm in the culture	Low selectivity, low efficiency	4-22	14-31
Vacuum fermentation	No fouling, easy to operate, no harm to the culture	Low selectivity Low efficiency	15.5-33.8	-
Perstraction	High selectivity, low toxicity to the culture	Fouling problem, emulsion and material cost	1.2-4100	7.7
Adsorption	Easy to operate, low energy requirement	High material cost, low selectivity, adsorbent regeneration	130-630	13-33

Table 1. 4-Comparison of various integrated processes for butanol recovery [9]

In Table 1.3 it can be noticed that this technique can't reach high butanol productivity. Despite all these methods are investigated, it is possible to say that only the distillation column can be used on a commercial scale, but the problem is the high operational cost, an alternative way can be the adsorption but nowadays it is used only in lab-scale [9]. In Table 1.4 pros and cons of these various techniques can be seen. For example, adsorption, that as said before could be the only substitute for distillation, has as distillation column high operation cost and also low selectivity. An important study of Kraemer et al. analyzed a hybrid integrated extraction-distillation process made up of:

- Liquid-liquid extraction unit
- Solvent distillation unit, the same authors identified also some good solvent for the process
- Further products distillation

Recently a new hybrid configuration composed using liquid-liquid extraction and divided wall column (DWC) column is proposed by Errico et al. [10], in this work different configurations are analyzed made up of:

- Liquid-liquid extractor
- Conventional distillation column
- Divided wall column.

First of all, the liquid-liquid extractor can be used to separate water from acetone, butanol and ethanol; then based on the configuration DWC or conventional distillation column can be used to separate the others component to obtain butanol as the main product [cf. Figure 1.1]. This study showed that among these different configurations the first, in figure 1(a), is the best in terms of total annual cost (TAC) but has a penalty for the Eco-Indicator 99 (EI99) compared to figure 2(c) [cf. Table 1.5]. Compared to the same configuration with two conventional distillation columns from this study, it is possible to analyze that in a hybrid configuration with DWC the value of TAC is lower of 16% compared to the hybrid extraction-simple column sequences. However, the EI99 value has a penalty of 11% respect the

oldest configuration because in DWC column heat is provided at higher temperatures.

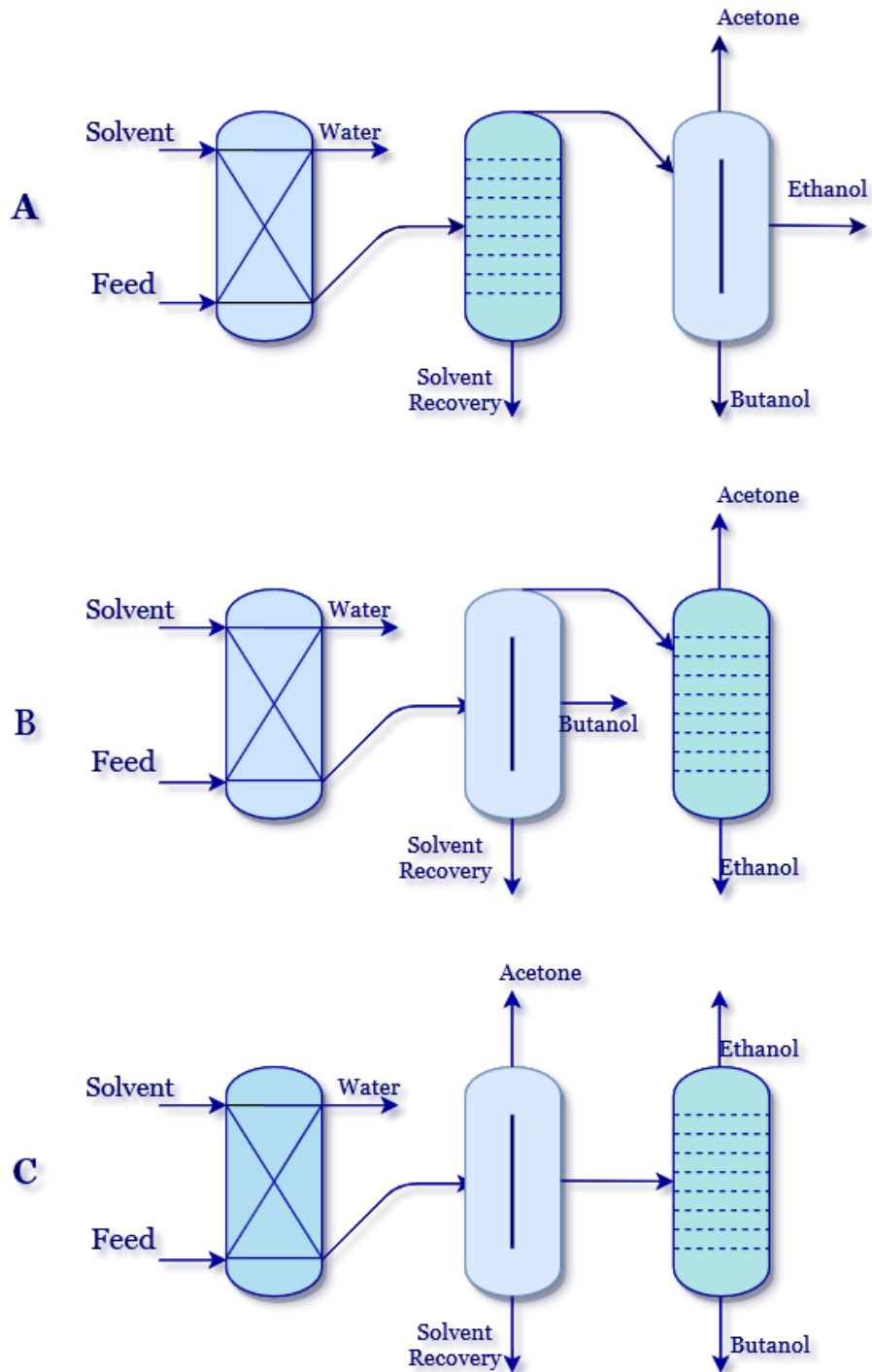


Figure 1. 1-Hybrid extraction DWC flowsheets [10]

Configuration	TAC [\$/y]	Condition number	EI99 [points/y]
A	11857	10.35	17.501
B	126683	12.070	20.829
C	128450	2.982	16.740

Table 1. 5-Objective function values for the configuration of figure 1 [10]

1.2 Divided wall column

In chemical engineering the leading separation process is distillation. This type of separation is capital and energy-intensive; Oak Ridge National Laboratory [11] in 2005 claimed that almost 53% of the total separation energy is used in the distillation operation of chemical and petroleum refining industries [12]. The huge economical problem has motivated the development of various types of fully thermally coupled distillation columns. Between these models, the divided wall column has gained wide acceptance for its single-vessel configuration different than the classical fully coupled model. DWC configuration ensures both spatial and economics saving, a ternary distillation can be realized in one column despite the classical two-units distillation sequence avoid the remixing problem. However, a real exploit of the divided wall column is not observed because this type of column works as the entire separation task. This leads to more difficulty in design and computation.

1.2.1 History and developments

The origins of the DWC date back in 1949 when Standard Oil patented the concept. After this, the leading companies in the sector started to exploit this new technology:

- in 2005 BASF reported more than 40 DWC in commercial service
- in 2006 Exxon Mobil announced the successful revamp of a tower that removes xylene from reformate
- Dow has operated an experimental DWC facility in Midland for about eight years

During this 70 years, much numerical expertise for the modeling of DWC systems has been developed and validated [13]. More than 120 DWC have

been installed worldwide, the majority for ternary systems. Development of DWCs for multicomponent, azeotropic, extractive and reactive separations are also reported, but implementations are limited. The component systems are often undisclosed [14]. Statistically, DWCs are used in many applications such as hydrocarbons, alcohols, aldehydes, ketones, acetals, amines and others [15].

1.2.2 Fundamentals

To better understand the potential of this configuration, let's consider an operation where the target is the separation of 3 generic non-azeotropic components A (light key), B (middle cut), C (heavy key).

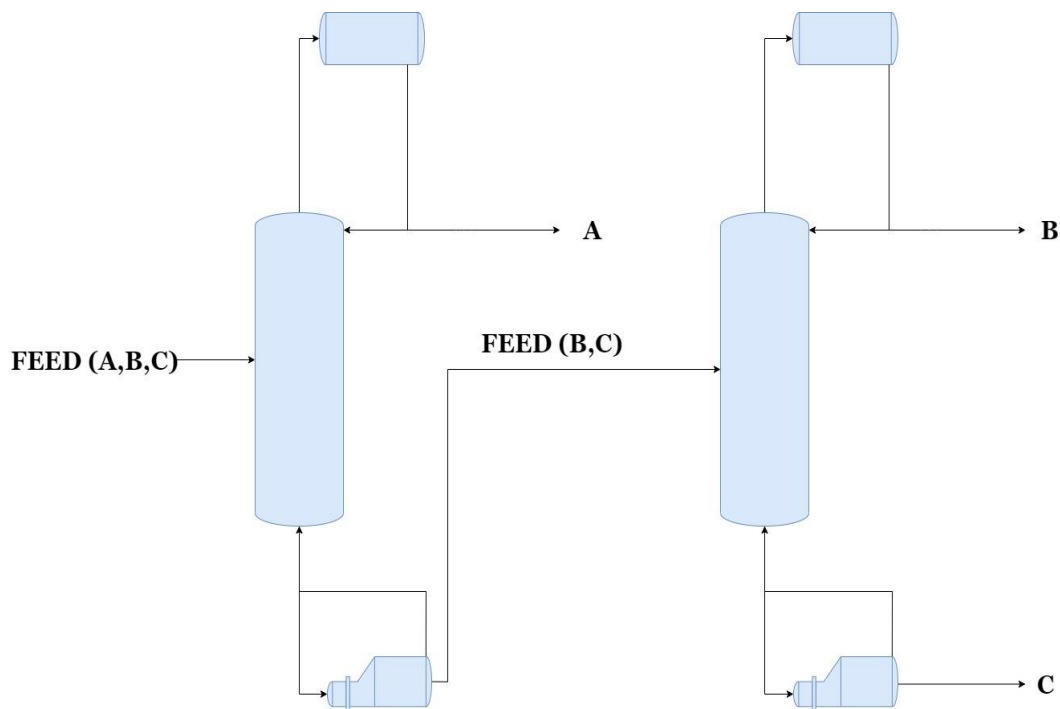


Figure 1. 2-Conventional two-column separation [16]

Process in conventional distillation is carried in 2 columns, the first removes one component (in this case the light key), and the second acts the separation of the remaining components. However, in the first column, the middle boiling component has a concentration peak near the center. As the concentration of C is increasing in the column bottoms, the composition of B is diluted due to the remixing effect [16]. These remixed components (B, C) will be separated with additional duty in the second column, it means that part of duty utilized in the first column is wasted thus lowering the energy efficiency of the system. It's important to say that also with the parallel configuration (the first column separates C and the second A and B), the remixing effect is not avoided.

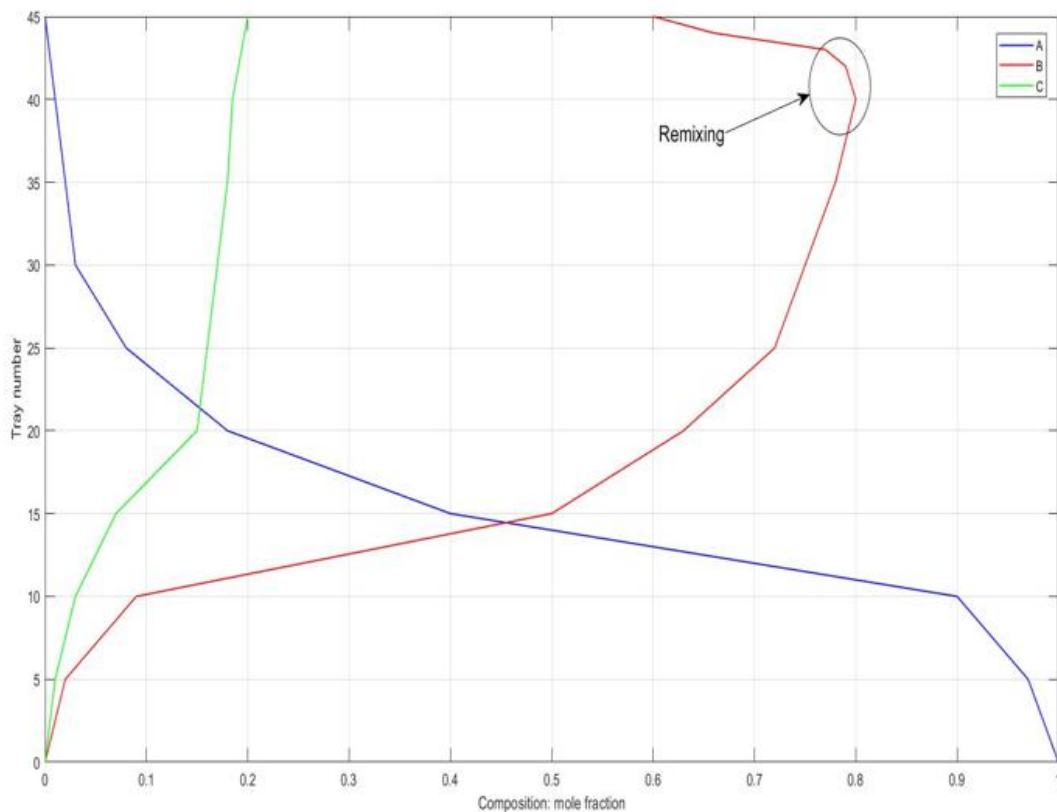


Figure 1. 3-Composition profile of a two-sequence column [16]

In Figure 1.3 it is possible to see the composition profile of components in a two-column separation, particularly it represents the proceeding of distillation in the first column. The heavy key A is pure at stage 0 while the lightest C reaches 0.4 mole fraction and is going to enter in the second column to reach the purity. The profile of B seems to reach 0.8 purity already in the first column but lowers its concentration due to the remixing effect, this step is avoided in a divided wall column. In the one-column process, the component maintains, during distillation, molar fraction profiles with increasing or decreasing monotonic functions without chemical behaviours that reduce efficiency. This is the most important difference and advantage for the DWC.

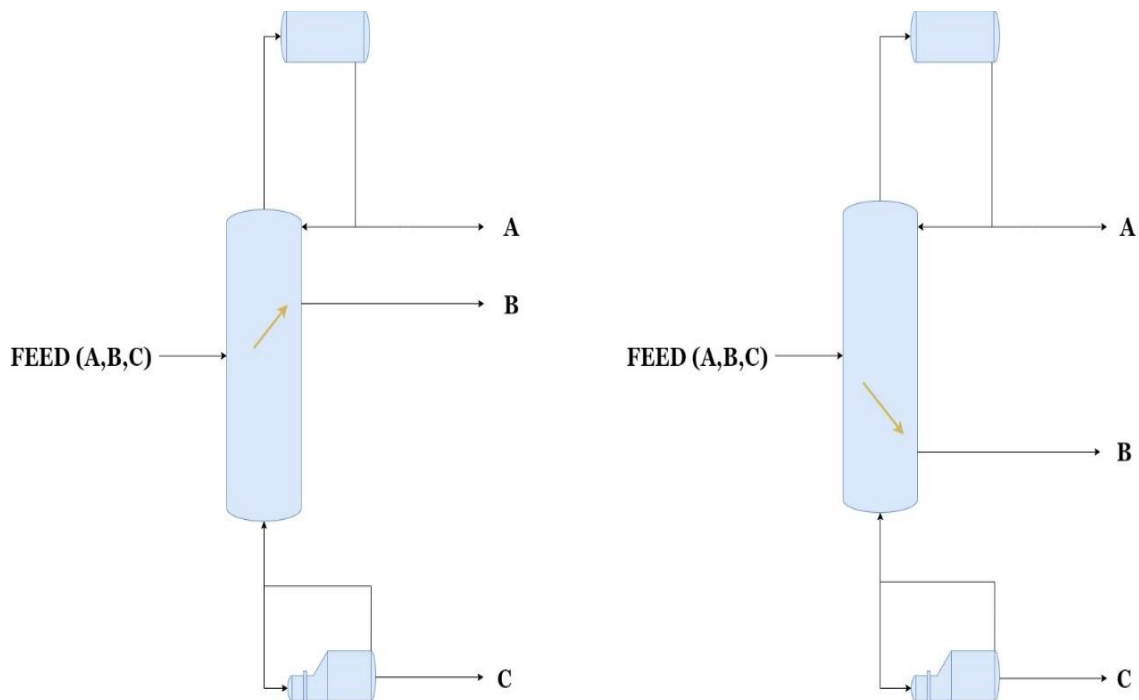


Figure 1. 4-Conventional two-column separation [16]

The same operation is made with a side-cut column, also, in this case, thermodynamic problems are present because the inlet feed has a remixing effect with the side-cut lowering the product quality. For side-cuts below the feed, heavier components end up in the middle cut affecting the final boiling point of the product. Likewise, a side-cut above the feed has problems meeting the initial boiling point.

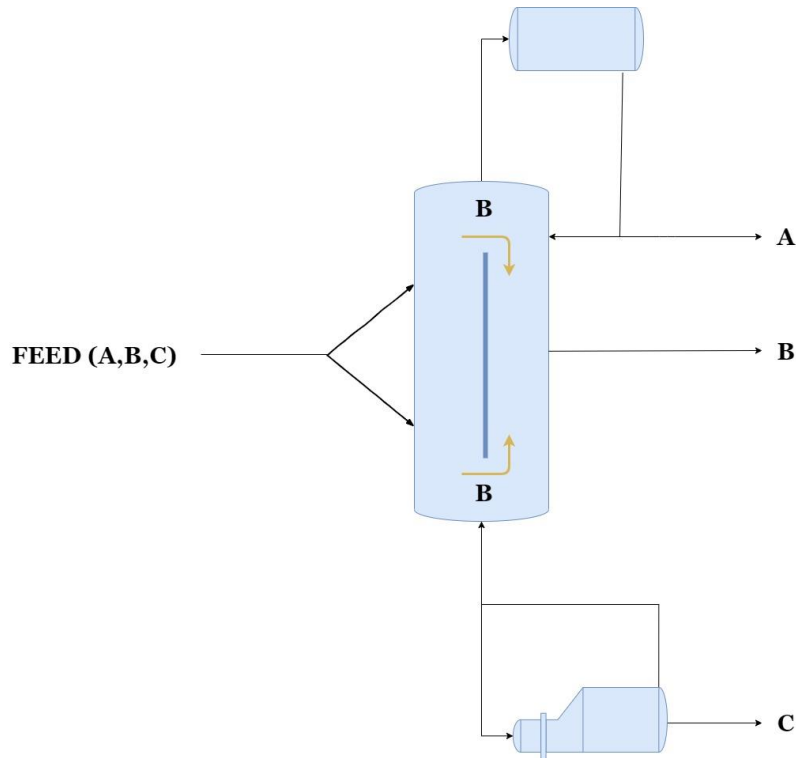


Figure 1. 5-Proprietary DWC [16]

A divided wall column is like a side-cut, the difference is the installation of a wall in the middle of the column. This separator avoids the remixing effect of the feed with the side-cut raising the product quality. The single column is split into 2 areas:

- pre-fractionator section, which helps to distribute the middle component among the lightest and heaviest key relating to its degree of volatility,
- main fractionator section, where the middle component is concentrated and removed.

The first section limits the duty waste until 30% than conventional distillation. Despite the advantages, DWC technology has had a slow growth in the chemical industries, only hundreds of DWCs have been installed. The cause can be traced back to the operability and controllability issues associated with the limitation of vapor split during operation. This technology requires more design variables than a conventional column such as a liquid and vapor split. Liquid and vapor split in DWCs is defined as the ratio of each

streaming flow into the prefractionation section to that flowing to the main fractionator. The unities that guarantee proper distribution of liquid and vapor flow to each section divided by the wall are called liquid and vapor splitters, they play an important role in the design optimization. The liquid split is easily manipulated with an active liquid splitter, several of those are already available and widely used (moving bucked type, manual reflux) [17].

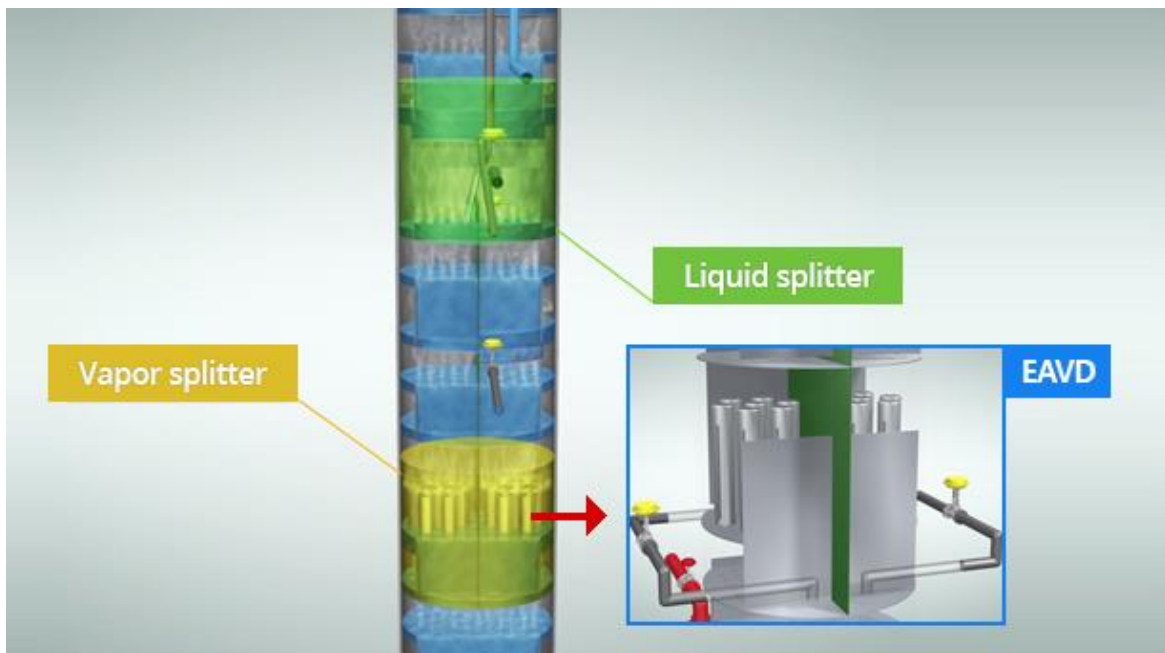


Figure 1. 6-3D representation of a liquid splitter in DWC [18]

Otherwise, the management of the vapor split is difficult, remains a serious challenge in the operation of DWC. For this reason, in most existing DWC's, the vapor splitting design is fixed for a specific area for vapor flow design, not a degree of freedom that could be modified during the operation. Such unities have an unfavorable loss in separation efficiency and result in higher reboiler duty. Vapor splits needs to be actively controlled so that the optimal vapor split ratio can be maintained in the occurrence of operation variations. Many studies for this problem have a direction in the active vapor splitter, different scientists proposed different technologies to find a practical solution [18] [19]. In developing an ideal internal flow-splitting device for DWC application, the following technical requirements should be considered:

- the device should not include a pump and moving unit,
- the additional volume contributed by the device should be small,
- the device should be able to manipulate and control the split ratio stably and accurately,
- the device should be simple, durable, and reliable.

The moving elements of the vapor splitter can be damaged by a continuous movement of the mechanical parts. Therefore, any vapor splitting equipment requiring an inserted axle and mechanical-electrical moving unit could have potential mechanical trouble and leaking and quaking problems, which would increase the capital and maintenance costs. The concerns associated with these potential problems might limit the real implementation of this type of vapor splitter in DWC [20].

One of the most consistent solutions proposed in recent years is the hydraulic driven active vapor distributor, associated with a mechanically driven vapor splitter. In this AVD model, the friction of the vapor flow path is hydraulically adjusted by changing the liquid level of a modified chimney tray.

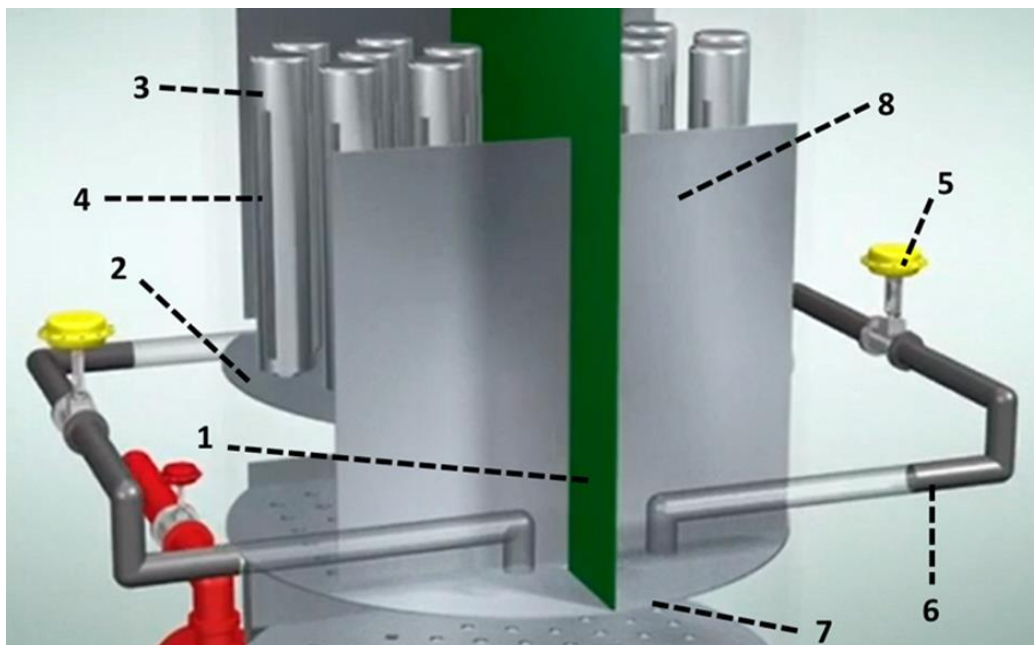


Figure 1. 7-3D representation of AVD [18]

For the sake of completeness, here below there is a list of pros and cons between a divided wall column configuration and a distillation train column.

Pro:

- Reduction of investment (up to 40%) and operational cost
- Lower energy consumption
- Less space required
- Back mixing effect avoided

Cons:

- Operation pressure between column sections is impossible,
- the higher temperature difference between cold and hot duties compared to a two-column set,
- more complexity of modeling, design, and control,
- Non-ideal mixtures require specific research.

1.3 Flexibility analysis and index

The standard procedure for chemical plant design consists of the assessment of the optimal design according to the economic and operational aspects. This methodology is usually strictly associated with a deterministic model that doesn't take into account uncertainty in the input parameters. In reality, the same process can have different working conditions according to variations in external variables (quality and quantity feedstock, product demands) or internal process parameters (such as kinetic constants, heat/mass transfer coefficients). ABE separation, like most of the biological process, deals with feedstock coming from biological reactions that have a high grade of parameter variations according to multiple factors [21]. Flexibility analysis is introduced to supply an optimum design which includes the probability that a perturbation could change the process performance. This type of study is a priori concept because it is built on the probability that some uncertain parameters may change. In the years, many authors proposed different indexes to analyze this concept. In 1985, Swaney and Grossman defined flexibility index, for a given design d , as the maximum fraction of the expected deviations δ that can be accommodated by the systems. Computation of flexibility index F_{sg} is made through the solution of these relations:

$$F_{sg} = \max(\delta) \quad (1.1)$$

$$s. t. \psi(d) = \max[\theta \in T(\delta)] \min(z) \max(i \in I, j \in J) f_j(d, z, \theta) \leq 0 \quad (1.2)$$

where ψ is a measure of feasibility of the system for a certain design and implies physical, legal, operational and economic constraints. If this value is lower or equal to 0, the design is feasible for each value of $\theta \in T$. The feasibility

analysis must be performed before the optimization flexibility problem. If F_{sg} result unitary the deviations $\Delta\theta^+$, $\Delta\theta^-$ can be fitted by the studied system. A graphical representation of the meaning for Swaney and Grossman index is proposed in the Figure 1.8.

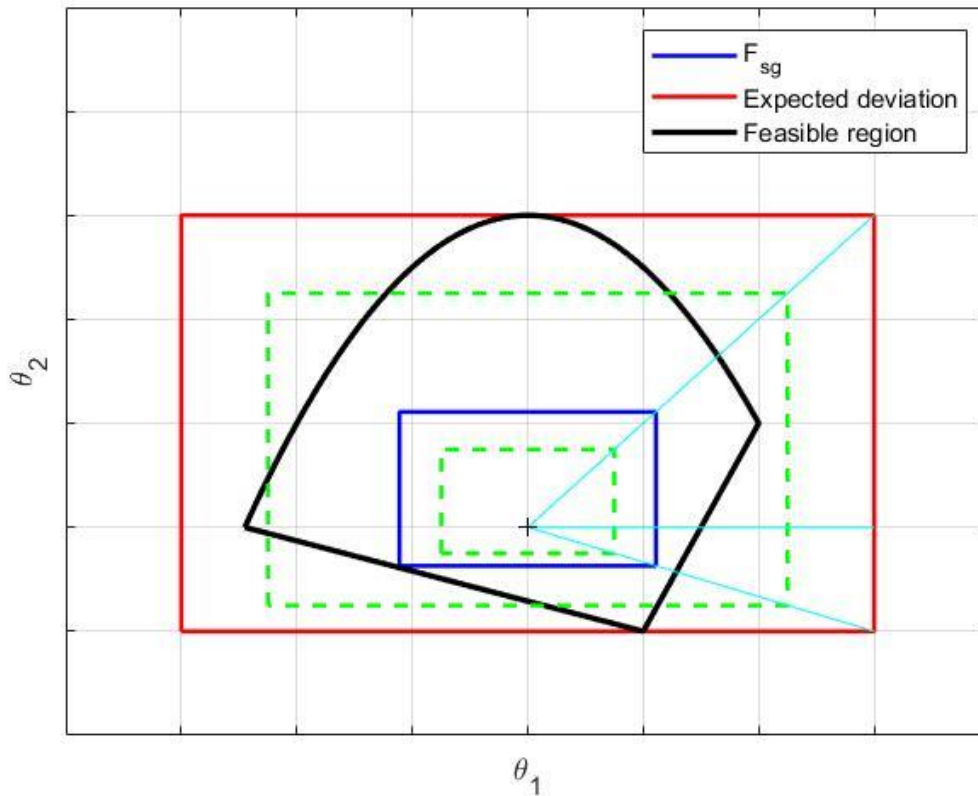


Figure 1. 8- Feasibility domain- F_{sg} [27]

Once feasibility analysis is performed, an optimization problem can be conducted (see equations 1.1). Swaney and Grossman [22] proposed two algorithms: a vertex search and an implicit enumeration scheme that avoids counting of all the vertex. The two algorithms are united by the identic assumption that the global solution lies at one of the vertices of the hyper rectangle [23]. In the same year, Morari et al. proposed the “resiliency index” as the capability of the system to easily recover or adjust to misfortune or change, similar to the definition of flexibility. RI expresses the largest total disturbance load and is independent of the direction of the perturbation. To

compute this index, the following system has to be solved.

$$RI = \min(i)\{|l_i^{max}|\} \text{ s. t. } \{max(j)f_j(\theta), \forall l : \sum |l_i| \leq RI\} \quad (1.3)$$

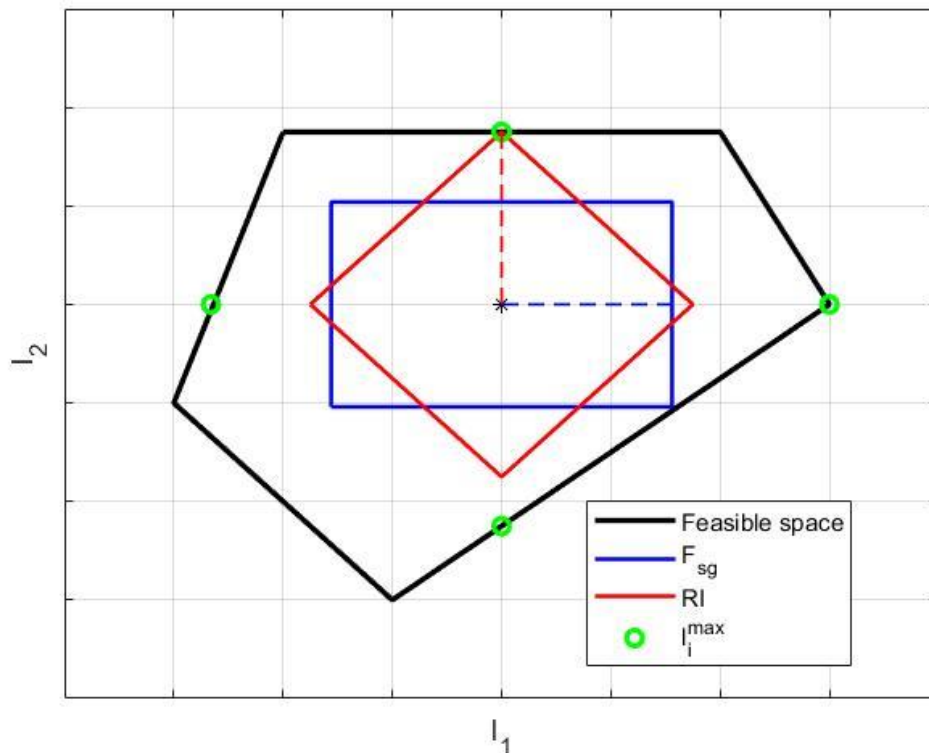


Figure 1. 9- Feasibility domain- F_{sg} vs RI [27]

The procedure to compute the RI index is similar to F_{sg} (search of the vertex) with the main advantage of the easier computational efforts, due to $2n$ vertices to compute respect to 2^n because of the geometrical analysis aimed to a polytope, no longer at hyperrectangle. The indexes previously explained are deterministic because doesn't consider that each possible operating condition has different probabilities to happens in the real world, so the flexibility analysis results rather conservative. In 1990, Pistikopolous and Mazzuchi [24] proposed a new concept of flexibility index based on stochastic

parameters. The original constraint space became the space of uncertainly dependent flexibility function thanks to the introduction of multi-cumulative variable distribution.

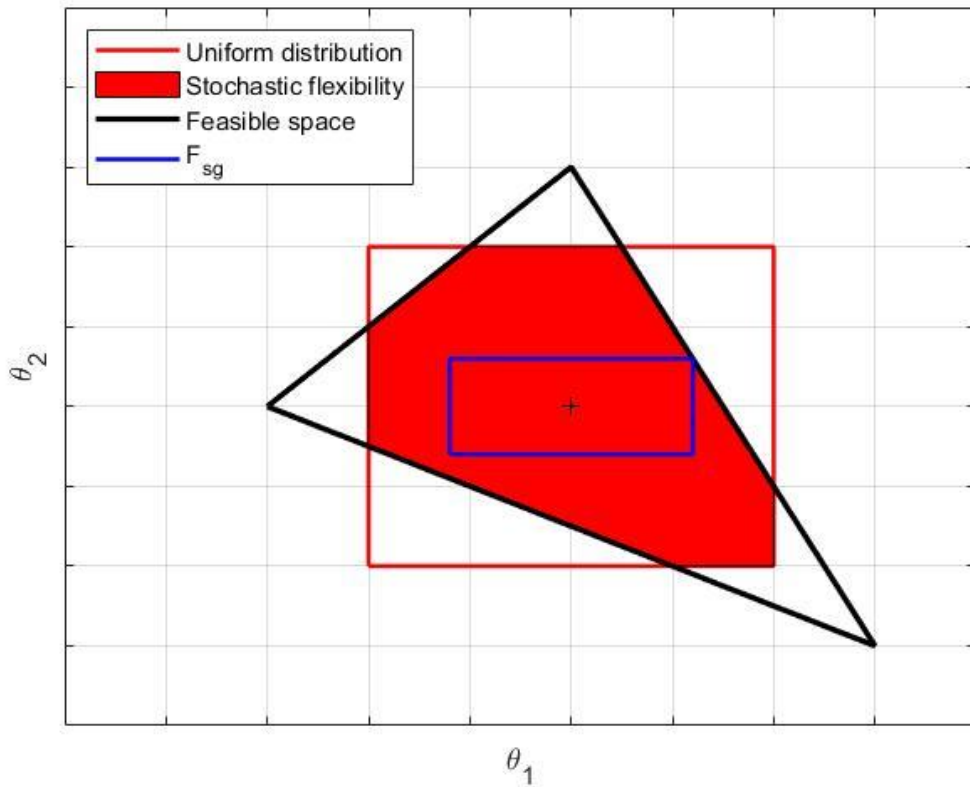


Figure 1. 10- Feasibility domain- F_{sg} vs SF [27]

SF , stochastic flexibility, index can be defined as:

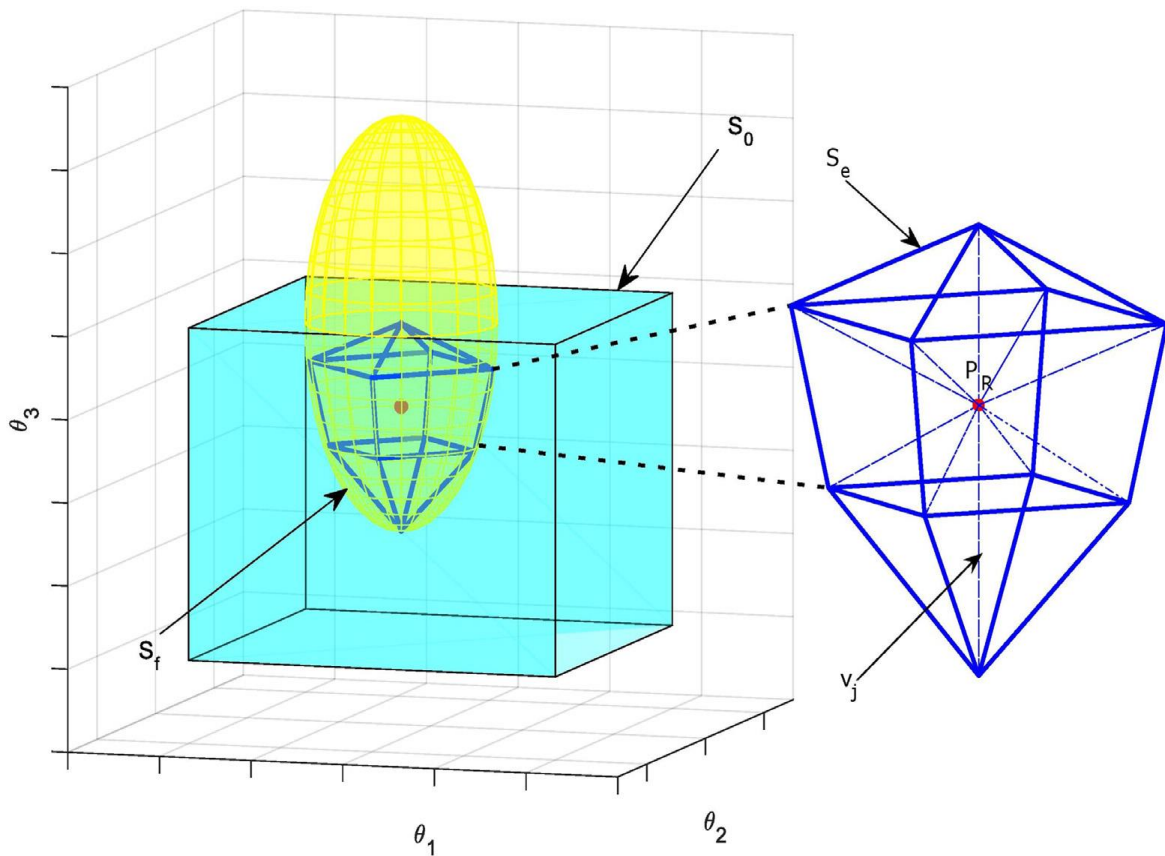
$$SF = Pr\{\psi(d, \vartheta) \leq 0\} = \int_{\theta: \psi(d, \theta) \leq 0} \dots \int P_D(\theta) d\theta \quad (1.4)$$

where P_D is the joint distribution function of the uncertain parameters θ . From Figure 1.10 is easy to understand the new point of view of Pistikopolous and Mazzuchi: the stochastic flexibility is not equally distributed (is not a definite shape) rather than Swaney and Grossman index. With this method,

a perturbation that is unlikely to happen has less weight in the computation of the processual flexibility. It seems clear that this technique requires the knowledge of the probability distribution data. In 1995, Dimitriadis and Pistikopolous [25] introduce the dynamic flexibility index (*DF*) for the optimization problem related to the dynamics system. To include the evolution of perturbations, the mathematical models have fundamentals in Swaney and Grossman model with the basic difference that the principal requirements are the association of θ and z with a time variable. Tuning and control loop are considered parameters for the evaluation of the system solution. Qualitatively, the *DF* index represents the maximum tolerated deviation of the system considering the variability of the feasibility domain: parameters that fit at a given time are not necessarily solution values in another time frame [25]. To reduce the complexity of the problem, some strategies are required, i.e. the assumption of uncertainty profile $\theta(t)$ is given. Lai and Hui, in 2008, proposed the most recent index that has the aim to overcome the problem related to the previous index; i.e the knowledge of the nominal point and the consideration of the critical uncertainty. This method requires less computation and available data. Lai and Hui's index are also known as volumetric flexibility index for its definition:

$$F_v = \frac{V_f}{V_o} \quad (1.5)$$

where V_f is the volume of the feasible space S_f and V_o the volume of uncertainty space. Usually, S_f has an irregular shape, so the computation of volume is very complex. The solution is the inscription inside S_f of a constructed space; with the careful choice of the shape of S_e , its volume can be used to estimate V_f .

Figure 1. 11- Feasibility domain- F_v [27]

As illustrated in the Figure 1.11, S_e can be constructed by first picking a reference point (P_R), which is not necessarily the nominal point, within S_f . The uncertain space can then be scaled based on this reference point and the expected parameter limits. Auxiliary vectors v_j can be radiated from the reference point in many selected directions; the points of intersection between these lines and the available space are joined, according to their position in space, generating the form of S_e [26]. Different forms of S_e can be generated, the estimation accuracy of V_f is made considering the selected model. Auxiliary vectors 3D position is bounded by the conditions written in equation 1.6. However, whether the feasibility domain is well defined and the constraints equations are known, there's no need to approximate anymore

since is possible to find the exact value of the S_f volume through multiple integrals; at the cost of a higher computational effort.

$$\max(x_j y_j z_j) V_e(x_j y_j z_j) \quad (1.6)$$

$$f_j(\theta_{ij}) \leq 0 \text{ and } 0 \leq x_j y_j z_j \leq 1$$

$$s. t. \theta_{ij} = v_{ij} l_j \Delta_{ij} + \vartheta_i^R, \Delta_{ij} = \begin{cases} \Delta^+ * \vartheta_i & (v_{ij} \geq 0) \\ |\Delta^- * \vartheta_i| & (v_{ij} \leq 0) \end{cases} \quad i = x, y,$$

CHAPTER 2

DIVIDED WALL COLUMN

After a little introduction on the divided wall column in the previous chapter, now it is important to study in deep the most important characteristic of this type of column, which will be the most important element of this thesis. In a particularly different configuration, degrees of freedom, design model and equivalent model will be analyzed.

2.1 Different configurations of DWC

Like conventional distillation, for three components separation, two different DWC configurations can be applied. The differences are in the location of the wall, feed and side draw. This element in the first configuration, most common and patented by Wright in 1949 [15], is placed in the middle of the column. In the second configuration, applied for the first time in 2004, the wall is located either at the lower or the upper part of the column. The column in Figure 2.1b is referred to as a *split shell column with a common overhead section and divided bottoms section*, while the column shown in Figure 2.1c is called a *split shell column with divided overhead section and common bottoms section* [28].

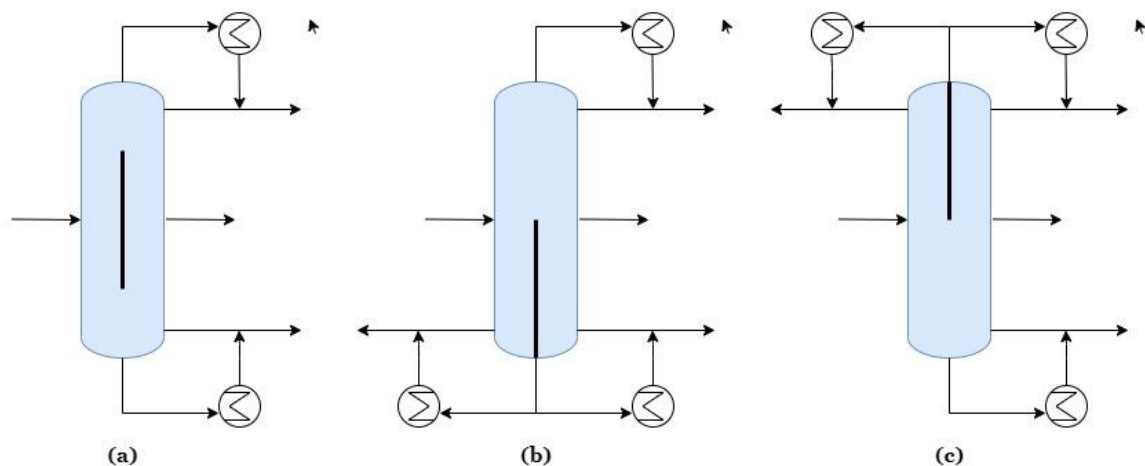


Figure 2. 1-Different configuration of the divided wall column. (a) wall in the middle of the column. (b) wall in the bottom section (c) wall in the upper section [36]

Other ways to have a different managing of the DWC are the shifting of the separator from the center towards the column walls or creating a diagonal section modifying the shape of the wall.

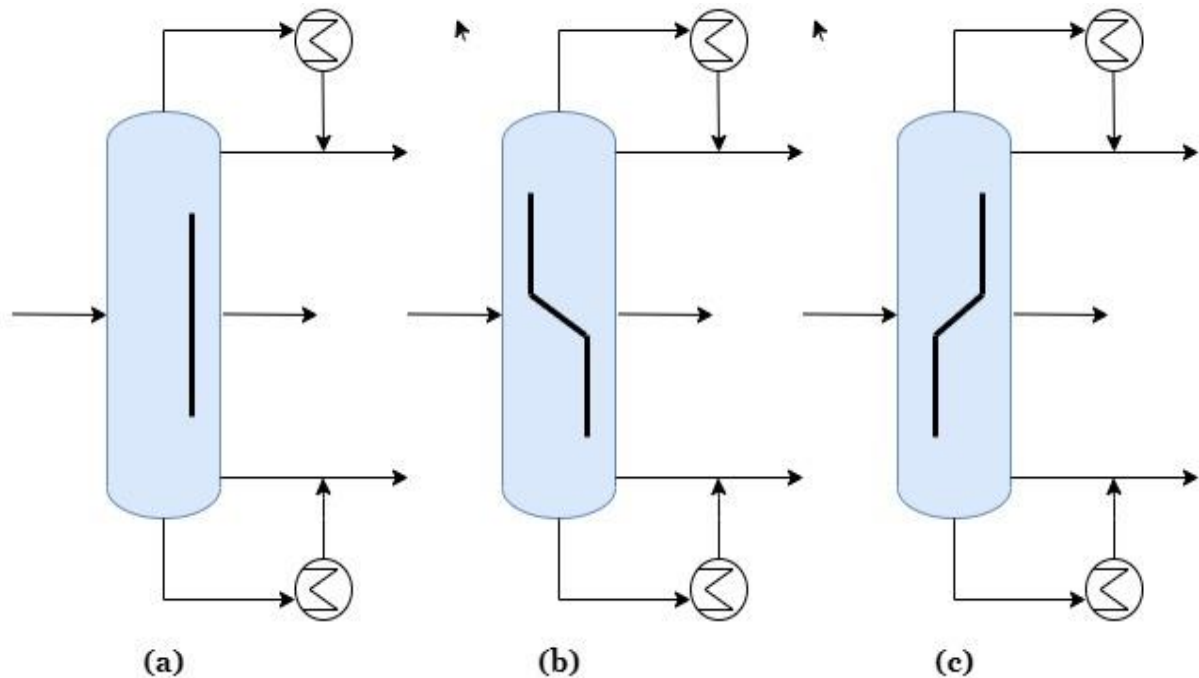


Figure 2. 2-Different configuration of the Divided wall column. (a) wall moved to the right of the column. (b) the wall creates a diagonal to the right in the middle of the column. (c) the wall creates a diagonal to the left in the middle of the column [36]

Divided wall column units can also be applied for the separation of more than three components, the number of configurations available grows with the number of compounds in the mixtures to split. The basic types used to lead such separations are the Kaibel column and multi-partitioned DWC, illustrated in Figure 2.3. In the Kaibel column configuration, illustrated in Figure 2.3a, separation is performed in a shell with one dividing wall [29] while the two middle-boiling products are accumulated at the righthand side of the dividing wall [15]. The great difference is in the number of the wall, on the Kaibel is used only one reducing the thermal efficiency which can be improved with the application of the multi-partitioned model. Figure 2.3 b represents the multi-partitioned configuration referred to as a *Sargent arrangement*.

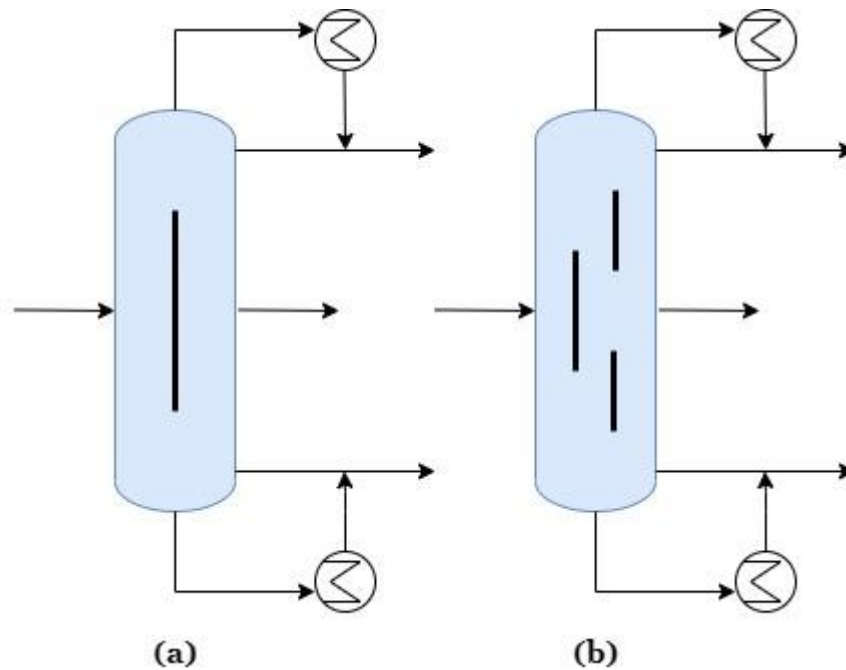


Figure 2. 3- Different configuration of the divided wall column. (a) Kaibel column. (b) Multipartitioned column [36]

In the past years, many arrangements for the separation of a mixture with more than three components were developed as needed by the chemical industry or the research. Selection criteria for the optimal column internals in another important aspect to analyze for the achievement of efficient heat and mass transfer and required purity. Generally, the decision criteria are similar to those of a conventional column, DWCs who treat heavier chemicals carried in vacuum conditions are all equipped with structured packing. BASF exclusively used packed columns while other companies, e.g. Koch-Glitsch and CEPSA refinery, install trays [30]. The selection of the internals implies different techniques for the wall construction which is more complex in the case of packed columns, especially for the welding. In the last years, non-welded technology was developed in cooperation between Montz and BASF. Using an unfixed separator makes the design much simpler and becomes installation faster and more precise [31].

2.2 DWC degrees of freedom

To achieve the aim of this thesis work is important to perform a simulation of a divided wall column with ABE mixture. For this purpose, it is necessary to have a set of specifications equal to the degrees of freedom of the column. Degrees of freedom is the expression used to define the variable that can independently change in a system. The definition of this quantity is:

$$d.o.f. = \text{number of unknowns} - \text{number of equations}$$

Since the degrees of freedom correspond to the number of variables that can change, this number also represents the maximum number of variables that can be controlled in the system. Indeed, is impossible to manipulate more variables than those who are free to change. Once the degrees of freedom have been analyzed the possible control configuration can be investigated with the Relative Gain Array analysis. Mutalib et al. [32] did the first important analysis of d.o.f. of a divided wall column. They use a method developed by Howard [33], based on the fact that degrees of freedom for a system is equal to the sum of degrees of freedom of all units of the system minus degrees of freedom of the interconnecting streams [32].

$$d.o.f. = \Sigma(d.o.f. \text{ of all units}) - \Sigma(d.o.f. \text{ of interconnecting streams})$$

In this study the divided wall column is represented with the Petyluk configuration (cf. Figure 2.4), it is possible divided the column into six sections with a cascaded tray, the column is composed by three feed and three side-draw trays located between the sections, there is also a total condenser on the top of the column and a partial reboiler on the bottom of the column.

The number of degrees of freedom for the column is:

$$d.o.f. = 3\sum NS(i) + NC + 35$$

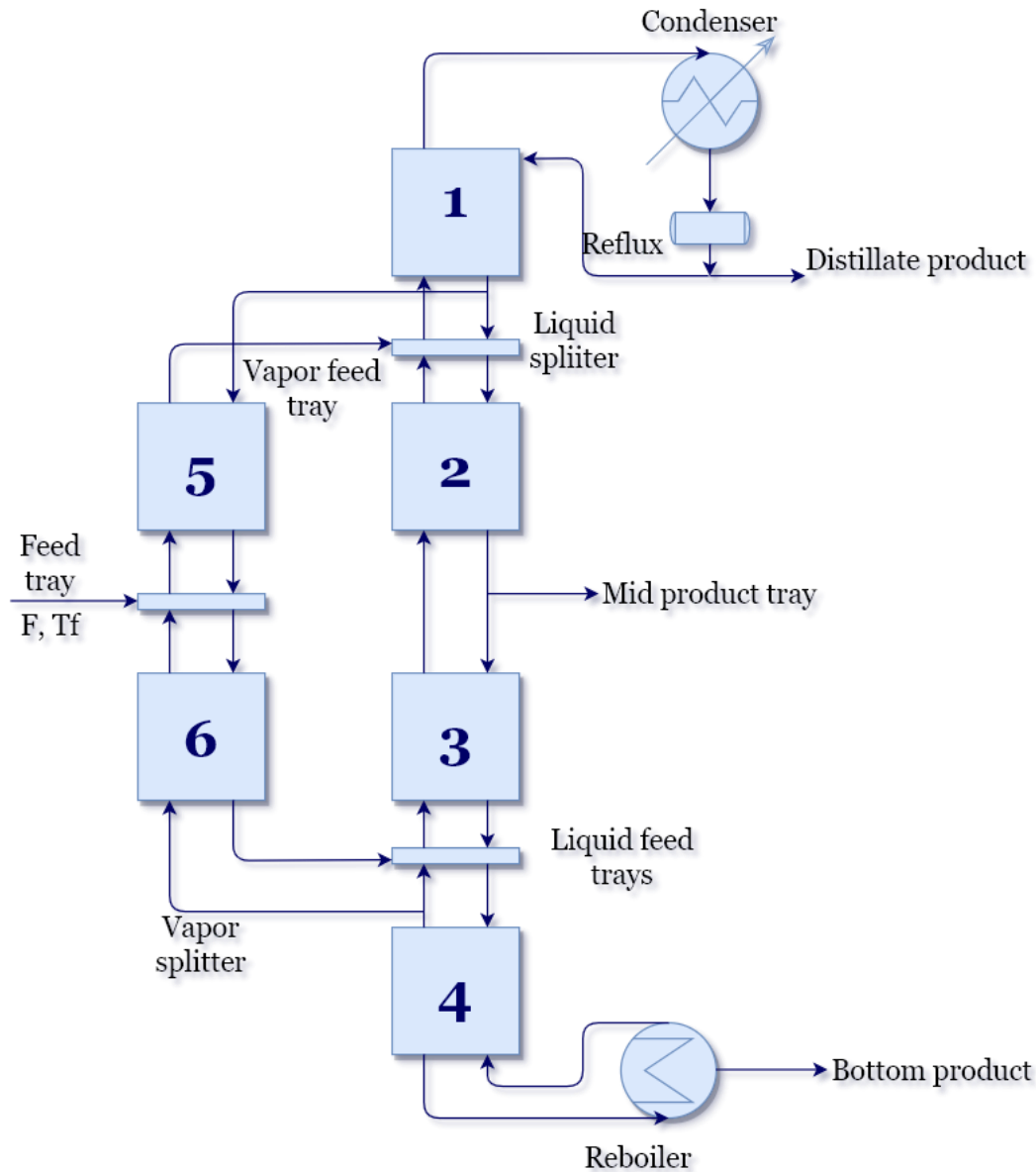


Figure 2. 4-Layout of Divided wall column used for degrees of freedom analysis [32]

Where NC is the number of the component in the column and NS is the number of stages for each section "i". Considering the product specifications and the inherent relationship the remaining degrees of freedom are $NC+10$, then fixing flowrate composition, flow rate and pressure, the final value is 9.

So, a maximum of 9 variables can be controlled to determine the system [cf. Table 2.1 and Table 2.2].

Units	Degrees of freedom
Top column	
Condenser/accumulator	NC+5
Reflux splitter	NC+5
Cascade of the stage (section 1)	3NT(1)+2NC+5
Vapor feed stage	3NC+9
Liquid feed stage	NC+5
Dividing wall section, Prefractionator side	
Cascade of the stage (section 5)	3NT(5)+2NC+5 3NC+9
Liquid draw stage	3NT(36)+2NC+5
Cascade of the stage (section 6)	
Main side	
Cascade of the stage (section 2)	3NT(2)+2NC+5
Liquid draw stage	NC+5
Cascade of the stage (section 3)	3NT(3)+2NC+5
Bottom column section	
Liquid feed stage	3NC+9
Vapor draw stage	NC+5
Cascade of the stage (section 4)	3NT(4)+2NC+5
Partial reboiler	NC+5
Total DOF	
	$3(NT(1)+NT(2)+NT(3)+NT(4)+NT(5)+NT(6))+27NC+87$
Restriction from 26 interconnecting streams	
	-26NC+52
Total DOF	
	$3(NT(1)+NT(2)+NT(3)+NT(4)+NT(5)+NT(6))+NC+35$
P. on all stage, Reb., Cond., and R. splitter	NT(1).....+NT(6)+9
Heat leaks on all stages and splitter	NT(1).....+NT(6)+7
The holdup on all stages	NT(1).....+NT(6)+3
N. of trays in each section	6
Feed (composition, flow rate, and pressure)	NC+1
Total DOF restricted	
	$3(NT(1)+NT(2)+NT(3)+NT(4)+NT(5)+NT(6))+NC+26$
DOF for the column	
	9

Table 2. 1-Detailed degree of freedom analysis for divided wall column [32]

Controlled variables	Manipulated variables
Feed Temperature	Feed preheater duty
Column pressure	Condenser cooling duty
Top product composition	Reflux flowrate
Middle product composition	Distillate flowrate
Bottom product composition	Side draw flowrate
Condenser/accumulator holdup	Reboiler duty
Reboiler holdup	Bottom product flowrate
Light impurity in the middle product	Liquid split at top of divided wall column
Heavy impurity in the middle product	Vapor split ad bottom of divided wall column

Table 2. 2- Controlled and manipulated variable for divided wall column [32]

The difference of degrees of freedom between divided wall column and conventional distillation column is 2, this number refers to vapor and liquid split ratio. Modeling a DWC is difficult to manipulate the vapor split and so it is left free to evolve naturally during the process, but on the other hand, the liquid split ratio can be manipulated. The manipulation of the liquid split ratio can be achieved with an external control on liquid streams returning to the top of the pre fractionator and the top of the column. The controller can be used with two different purposes:

- To fix the two flows with a specific relation, in this case, an internal mechanism is fixed on the top of the DWC to separate the mixture in two streams headed for each part of the column;
- To vary the two flows.

It is important to know that the manipulation of the liquid split ratio corresponds to manipulation on the reflux ratio of the column, to reach one of the specifics. [32]. Most recently Woff and Skogestad [34] have considered that the pre fractionator has zero degrees of freedom, and, on the other hand, the main column has five degrees of freedom, this analysis was done considering the pressure constant. These five degrees of freedom are:

- Reflux flow
- Boil up flow
- Side draw flow
- Liquid split ratio
- Vapor split ratio

Also, in this case, as for Mutilab [32], liquid and vapor split ratios are considered to minimize the reboiler duty, while the other DOF is used to reach product purity [35]. In the last years, an important study of Ling and Luyben considers only four degrees of freedom for DWC, this number is obtained considering that the vapor between the two-stream is divided proportionally and pressure is considered a fixed parameter. The analysis of Sangai et al [35]. applied the conventional MESH equation, plus the pressure drop equation, obtaining the MESHD equation. The term MESH equation refers to the sum of mass and energy balances, phase equilibrium relations and mole fractions summations. Considering a DWC column, for applying MESHD equations the trays are numbered from top to bottom, so condenser is trays 1 and reboiler is stage N . The first tray of section 1 is $Ns1+1$ and the last tray of section 1 is $Ns2$. As far as concern section 2 the first tray is $N+1$ and the last one is N_T .

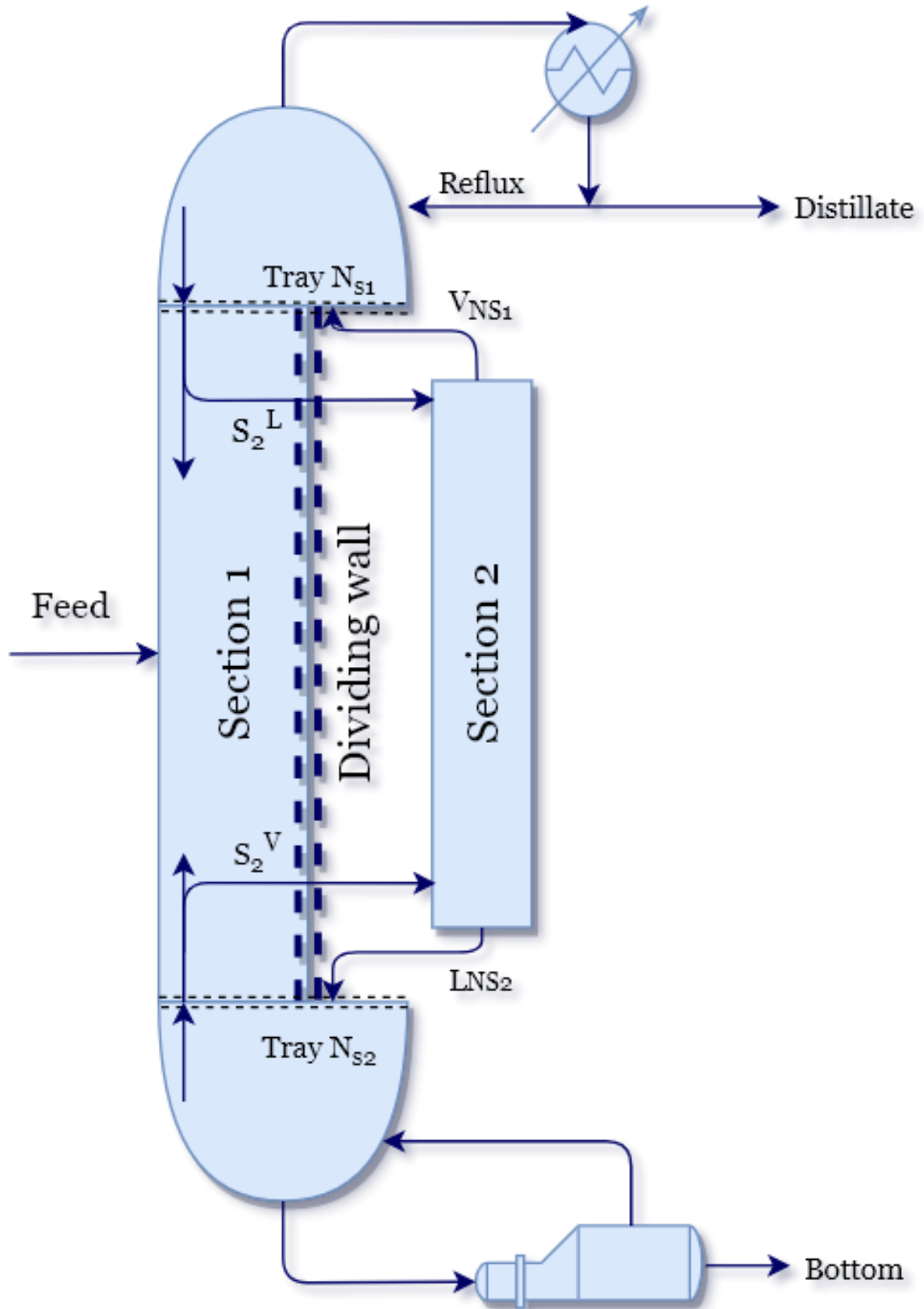


Figure 2. 5-Divided wall column with an explanation of different section [34]

In the previous Figure 2.5, it is possible to see that the trays between 1 and N_{S1} are full trays, and trays between N_{S1} and N_{S2} are divided between sections one and section two, these trays correspond to the length of the dividing wall. Despite the pre-fractionator is shorter than the main column this column is containing in a single vessel as high as the main column. With this method, the first divided trays are called N_{S1+1} in section one and $N+1$ (second half of the tray) in section two.

The total number of trays is $N_T = N + (N_{S2} - N_{S1})$ while the number of trays of section 2 is only $N_{S2} - N_{S1}$. As far as concern the different streams of the column these are:

- Total distillate product (D).
- Liquid stream originating from trays N_{S1} , it is divided into two parts. L_{NS1} goes to tray $N_{S1} + 1$ while S_1^L that goes to $N+1$ (the second half of the stage N_{S1}).
- Vapor stream originating from trays N_{S2} is divided into two parts. V_{NS2} going to tray $N_{S2}-1$ and S_2^v going to N_T .
- Lateral stream rich in medium component, exit from the middle of section 2 (S_3).
- Total bottom product (B).

This scheme makes a Divided wall column as a pair of two thermally coupled distillation columns, in which the main section is section one with condenser and reboiler and section two is the post (or pre) fractionator. The equation for the resolution of a DWC with three streams are the same as a classic distillation column, with the only differences of these equations:

- Component material balance equation (with j from 1 to C)

$$l_{NS1-1,j} + v_{NS1+1,j} - l_{NS1,j} - v_{NS1,j} - R_1 l_{NS1,j} + v_{N+1,j} = 0 \quad (2.1)$$

$$R_1 = \frac{S_1^L}{L_{NS1}} \quad (2.2)$$

$$l_{ns2-1,j} + v_{NS2+1,J} - l_{NS2,J} - v_{NS2,J} - R_2 v_{NS2,J} + l_{NT,J} = 0 \quad (2.3)$$

$$R_2 = \frac{S_2^V}{V_{NS2}} \quad (2.4)$$

- Enthalpy balance equation

$$\begin{aligned} L_{ns1-1}h_{NS1-1} + V_{NS1+1}H_{NS1+1} - L_{NS1}h_{NS1} - R_1L_{NS1}h_{NS1} \\ - V_{NS1}H_{NS1} + V_{N+1}H_{N+1} = 0 \end{aligned} \quad (2.5)$$

$$\begin{aligned} L_{NS2-1}h_{NS2-1} + V_{NS2+1}H_{NS2+1} - L_{NS2}h_{NS2} - R_2L_{NS2}h_{NS2} \\ - V_{NS2}H_{NS2} + L_{NT}H_{NT} = 0 \end{aligned} \quad (2.6)$$

- Pressure balance equation, considering the difference of pressure of two different sections:

$$(P_{NS2} - P_{NS1}) - (P_{N1+1} - P_{NT}) = 0 \quad (2.7)$$

This equation is used as a balance of pressure between the two sections and the two streams that go in section 2 (S_1^L and S_2^V). So, it is possible to say that the degrees of freedom of DWC using this method is only one more than that obtained from a distillation column (cf. Table 2.3).

N. of equation	Ind.variables	Dep.variables	N.of ind.variables	N.of dep.variables
1-4,21,23,23	$L_{i,j}, v_{i,j}, F_j, S_3, S_1^L, S_2^V$	R_1, R_2	$2N_T C + C + 3$	$N_T C$
5 and 8	-	L_1, V_1	-	-
7 and 8	$(T_j)_{j=2...NT}$ $(P_j)_{j=2...NT}$	$K_{i,j}$	$2N_T C - 2$	$N_T C$
9-13,22,25,26	R, Q_C, P_1, Q_B, H_F	H_j, h_j	5	$N_T + C$
14,19,27	-	$H_{Ti}, \Delta P_{rc}$	-	N_T
15-18	-	$(h_{ow})_l, (h_d)_l, (h_f)_l$	-	-
-	-	-	$2N_T(C+1) + C + 6$	$2N_T(C+1)$

Table 2. 3-Independent/dependent variables for DWC [34]

As it is possible to see in Table 2.3 the difference between the number of independent variables and the number of independent equations is $C+6$, but if $C+2$ variables are known (feed properties and condenser pressure) the degrees of freedom of a DWC with fixed trays and three streams are four, one less from the previous studies investigated in this thesis. Considering the definition of degrees of freedom with these four independent variables it is possible to find all the unknown of the previous balance equation. The parameters that help to reach convergence are the same as the previous analysis.

2.3 Design of DWC

As far as concerns the design of DWC prior to the 21th century there is no available information. The first public informations became available when it was produced outside BASF [36]. A theoretical analysis of DWC made by Petyluk [37], concludes that the work of this column can be extended to the separation of a different number of components, following these rules:

- In each column section, the key components are the components with extreme volatilities, which can be the lightest or the heaviest. For this reason, a column needs $n(n-1)$ sections for the separation of n component, differently from the conventional scheme in which $2(n-1)$ sections needed.
- Independent of the number of components only one reboiler and one condenser are enough.
- All n products can be obtained with high purity.

DWC column is thermodynamically equivalent to a Petyluk column, but it is considered as a single shell realization of a Petyluk column [36]. To do an optimal design of a DWC it is necessary to have an adequate model and computer-based simulations, that commercial process simulators don't have. So, various method of decomposition of DWC was proposed in the past years [38]. The first step to designing a DWC column is like a conventional distillation column design method, it necessary to choose:

- Column configuration
- Operating pressure
- Appropriate VLE model

The next steps are different from a conventional distillation column. They consist of:

- Establishing initial configuration
- Short-cut or detailed design of the column
- Choice of stage and reflux
- Optimization
- Equipment sizing
- Process and control system.

2.3.1 Heuristic Rules

To ensure the convergence of the simulation the design parameters require a good initial value and some guidance [39]. The following list of heuristic using in this study is proposed by Becker, Godorr, and Kreis [40]:

- Design a conventional two-column system as a base case, for example, an indirect sequence.
- The total number of stages for DWC as 80% of the total number of stages required for the indirect configuration:

$$N_{DWC} = 0.8 * (N_1 + N_2)$$

- Place the dividing wall in the middle third of the column (33-66%)

$$Wall = 0.33 * D_{column}$$

- Reboiler and condenser duty is determining as 70% of the total duties of two conventional columns:

$$Q_{dwc} = 0.7 * (Q_1 + Q_2)$$

- Use equalized vapor and liquid splits ($r_v = 0.5$, $r_l = 0.5$) as initial values.

These parameters are good only for the first approach to a DWC column design. For a rigorous design, a certain level of experience is needed. Intact it is computationally demanding, depends on the configuration chosen and on the modeling approach [36] .

2.3.2 Approximate design method

The first DWC design approach was published by Triantafyllou and Smith [41], and it was based on the Fenske-Underwood-Gilliland-Kirkbride (FUGK), each one of these models has a different aim [39]:

- Fenske: minimum number of equilibrium stage
- Underwood: minimum reflux
- Gilliland: stage requirement at a chosen operating reflux ratio
- Kirkbride: Feed stage for a given separation

The FUGK model has two basic assumptions:

- Constant relative volatility
- Constant molar flows

Another similar method, also in this case a short-cut, is proposed in 2002 by Muealikeishna, Madhavan, and Shah [42]. Their method is very useful since it proposes a visualization tool in which is possible to see all the configuration in only one plot. Moreover, this tool can be also used for a simple optimization procedure. The most important characteristic of this method is that the calculations are simple and can be used for mixtures of different numbers of components, as in this thesis case in which the component of the ABE/W mixture is four (acetone, butanol, ethanol, and water) instead of three [43]. Differently from the method of Triantafyllou and Smith of 1994, in 2001 Amminudin and Smith [44] supported that using the Kirkbride equation to find the thermal coupling location, it brings to some errors in the rigorous design. They proposed a method that can be considered semi-rigorous based on an equilibrium stage composition concept that was previously applied for the synthesis of the azeotropic distillation. This method starts with the definition of product composition and follows the opposite path to find the

specification to find them. This method is certainly more accurate than the previous one, but on the other hand, it was more complicated from the computational point of view, for this reason, the Triantafyllou and Smith method was preferred in literature for its simplicity. More recently, Sotudeh and Shaharaki in 2008 [45], proposed a new method that uses only the Underwood equation. They considered useless the Fenske equation that can be used to find the minimum number of the stage in a column. This choice has a reason: indeed, the Fenske equation is based on the assumption of equal vapor and liquid composition on the bottom and top of the column, and this assumption can't be considered for the pre-fractionator in a DWC. The last approach was proposed by Rangaiah, Ooi, and Premkumar in 2009 [46]., their procedure uses AspenTec HYSYS[®]. This method is based on the assumption of equilibrium on the stage of the column, but it needs some experimental data such as the efficiency of the column for a trays column or HETP value for a packed column.

2.3.3 V_{min} diagram method

Halvorsen and Skogestad [47][48], proposed a method based on a graphic in which the minimum energy is represented by normalized vapor flow, as a function of the feed distribution. Also, this resolution is based on Underwood's equation and it uses some assumption:

- Constant molar flows
- The infinite number of stages
- Constant relative volatilities.

Although this approach is really useful it can be used only with the zeotropic mixture. Moreover, it needs some parameters:

- Feed composition

- Feed quality expressed by the liquid fraction
- K-values
- Desired product purities or recovery ratio.

The V_{min} diagram conveniently shows the vapor and liquid flow in every column section, which can help in a rigorous design of the column. This method is based on the assertion that the minimum vapor flow required for the separation on n component in the feed to n pure component in the product. The peak of the V_{min} diagram corresponds to the energy requested for the most difficult binary split. It is possible to see in Figure 2.6 in the diagram plots the vapor flow rate above the feed (V/F) versus the distillate flow rate above the feed (D/F), the recovery of the product and the composition of the product are determined. Using the Fenske equation is possible also to find a preliminary number of stages, starting from N_{min} finds with the Fenske equation, the number of trays is conserved twice of N_{min} . As far as concern the enthalpy of the mixture it is found with the liquid fraction (q) [39].

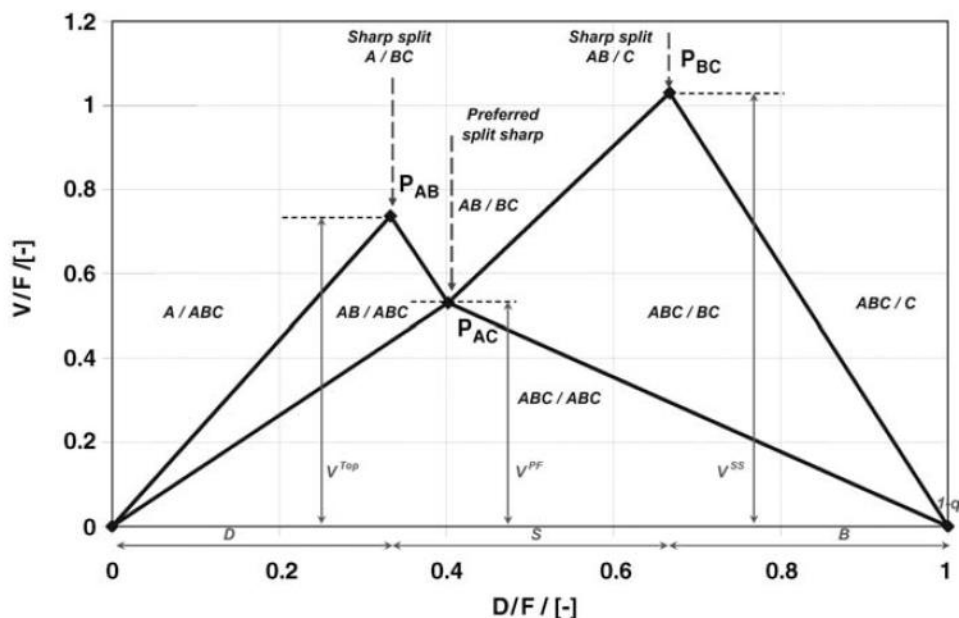


Figure 2. 6- V_{min} of an ABC ternary mixture [36]

In this figure, a ternary mixture ABC is showed the product is divided into top and bottom products in a simple two-product “infinite stage” distillation

columns as a function of the operating point. In the diagram is possible to see three peaks that correspond at the value of V/F above the upper boundary, at this point, the column is over-fractionating, so the valuable energy is wasted [36]. With this method, all the necessary information for rigorous design, such as an internal flow rate of vapor and liquid in different columns section can be easily calculated by the graphic [39].

2.3.4 Optimal Design of a DWC

Optimal design for a DWC column was proposed in 2011 by Dejanovic et al. [39]. This method gives the possibility to calculate the reflux requirement and several trays for a three product DWC but can be extended easily to another type of DWC, such as more component DWC, azeotropic, extractive and reactive distillation. The steps of this method can be seen in the previous Figure 2.7 and are:

1. Define the aim of the distillation: feed composition, feed state, a key component, recovery of the key component.
2. Calculate, for an infinite number of the stage (for example $N > 4N_{min}$, with N_{min} calculated with Fenske) and for a different possible binary split of key component the reboiler flow rate and distillate flow rate.
3. Use the V_{min} graphic to find the product, the internal liquid flowrate, and the internal vapor flow rate.
4. Starting with a rigorous simulation using values from the V_{min} diagram, and then it is necessary to change the number of trays for each column section.
5. Adjust the vapor split ratio and liquid split ratio, with the reboiler duty, minimized, and the purity of the product maximized.

6. Repeat this calculation by re-initialization, reducing step after step the number of trays in each section until $N(R_R+1)$ is minimized.

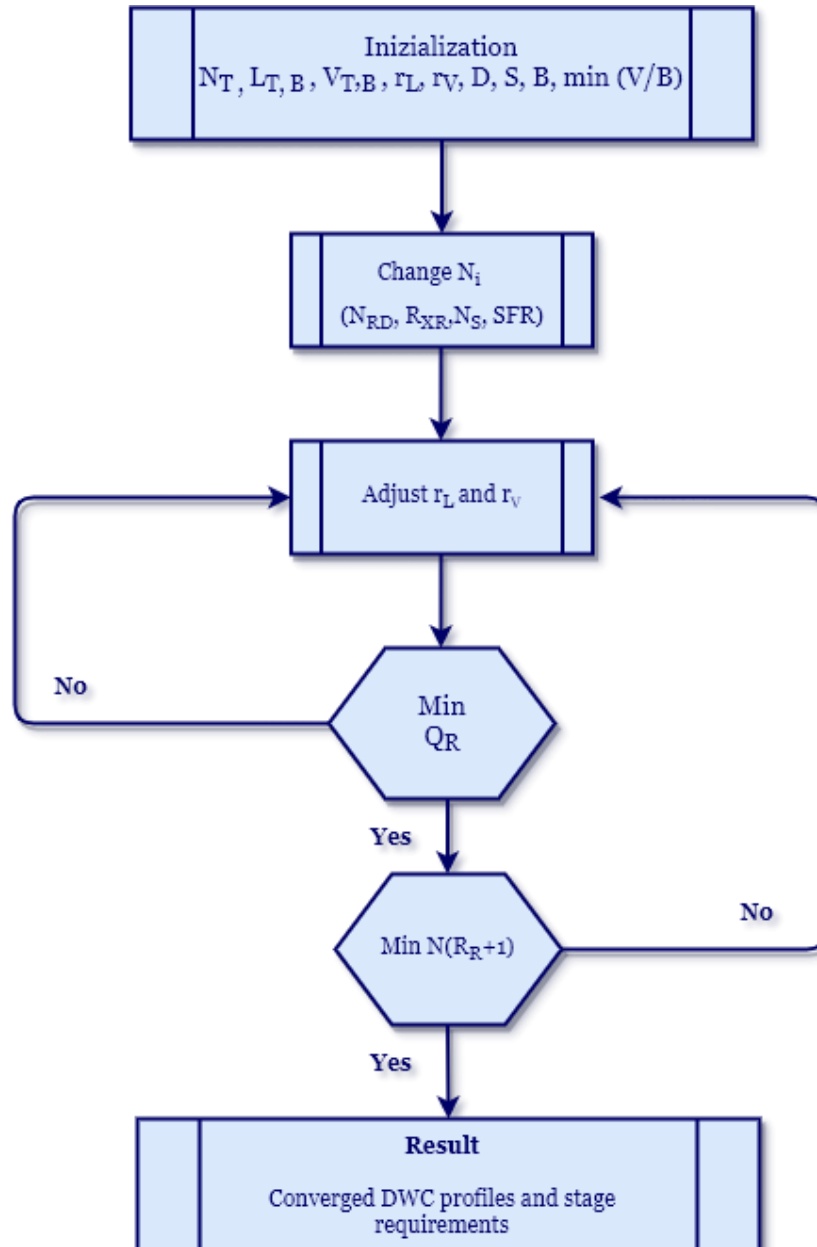


Figure 2. 7 Algorithm of detailed DWC modeling for optimal design simulation [36]

2.4 Equivalent models

Unlike conventional distillation columns, DWCs have more degrees of freedom when conducting design and simulation, for this reason, there aren't libraries with standard DWC shortcuts in commercial software packages, such as Sim Central, Pro II, Aspen Plus®, ChemCAD or Aspen HYSYS®, that can be used directly for design and simulation. An optimal solution is the arrangement of conventional distillation columns in sequence to simulate DWC's. The most used model is a pump-around model, the two-column sequence model, and the four sequences model.

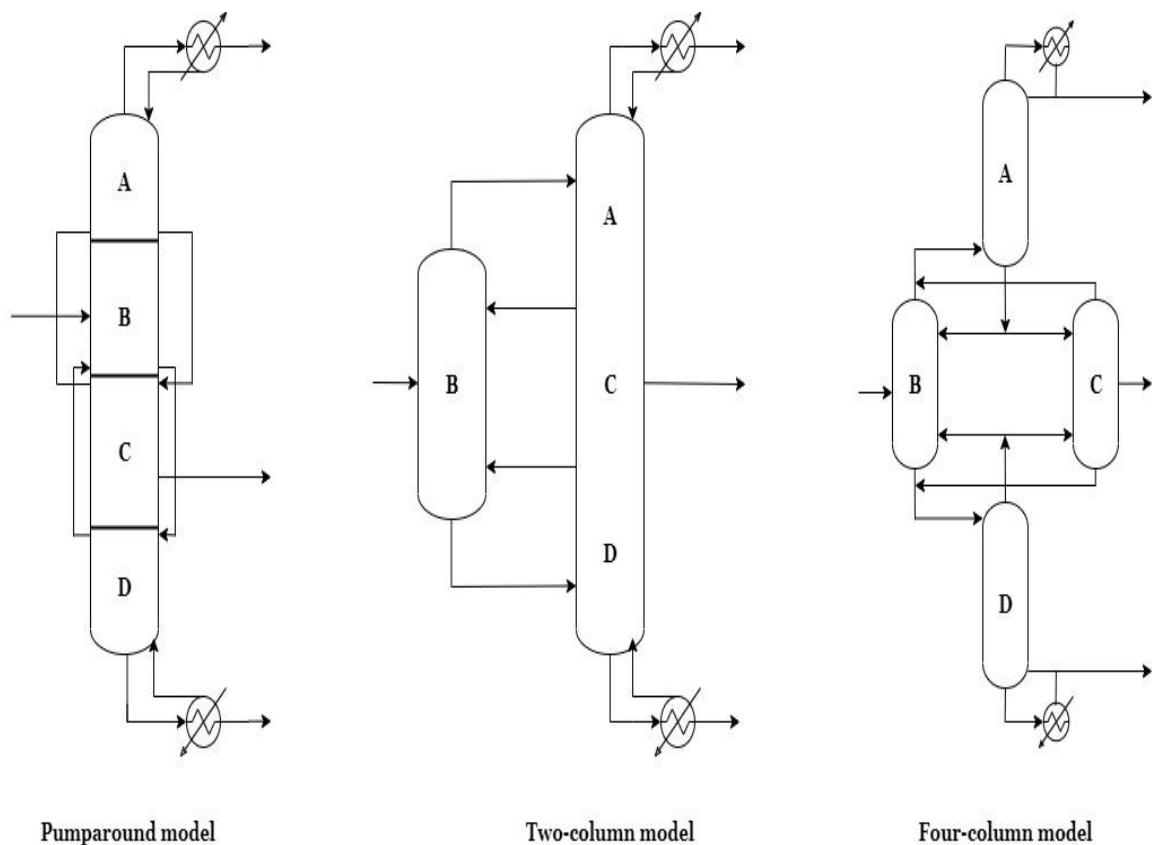


Figure 2. 8- Schematic diagrams of different equivalent models: (a) Pumparound, (b) two-column model, (c) four-column model [12]

The *pump-around* model connects the four sections of DWC vertically, the numerous side cuts work in order to link section not physically joined in such a way to resemble the structure of a column that has pump-around. It is computationally simpler and easier to initiate than other arrangements since it involves simulating only one column conveniently carried out in any process simulator. However, it has been reported that this configuration can cause convergence problems because liquid and vapor streams could be reset to converge the simulation [40]. The convergence of simulation is reached when all the model equations written in the simulator are calculated and solved, that doesn't mean it has a physical consistency relative to our simulation objective. The *two columns sequence* uses the same structure of a Petlyuk column, it is a configuration with a column without duties connected to a normal distillation column, between the two are interconnected four streams. Sometimes it is used because is easy to set up and is more flexible than a pump-around configuration. Despite these benefits, this arrangement strictly required good initializations of the interlinking streams; otherwise is hard to reach the convergence. Dejanovic, Matijasevic, and Olujic [39] recommend the following procedure to initialize such sequence:

- Specify the composition of the coupling streams, and the flows from the pre-fractionator to the main column in the following way:
 - Set the vapor stream composition using the feed stream composition with all impurities (heavy components) set to zero. Keeping the same composition, set the total flow rate as determined by the short-cut model. Set the temperature as the dew-point temperature at the operating pressure.
 - Set the liquid stream composition using the feed stream composition with all impurities (light components) set to zero. Keeping the same composition, set the total flow rate as determined by the short-cut model. Set the temperature as the boiling point temperature at the operating pressure.

- Run the main column once as standalone, using the boil-up ratio calculated by the short-cut method and highest reflux ratio from the direct sequence, for reboiler and condenser specifications.
- Run the pre-fractionator column once, as a standalone unit.
- Run the entire sequence together, using these converged profiles and the composition of the coupling streams and setting the desired distillate and bottom product purities for the condenser and reboiler specifications, respectively.

The *four columns* model represents the four sections of a DWC: top common rectifying section, feed side section, side streams section and bottom common stripping section. This model has greater flexibility than others and is the one that best reflects the DWC configuration, but is the most difficult to initialize, as more interconnecting streams need to be estimated and is also slowest to converge [14].

The parallel column model described using the equilibrium stage concept, meaning that the vapor and liquid flow leaving a stage are assumed to be in equilibrium. In the figure below, a schematic diagram of three stages at the top of a dividing wall, with notations introduced. It is worth emphasizing that for conventional columns there are no such interlinking streams, while in divided wall columns only a few such connecting mass streams exist. In the figure is also important to consider the variable $Q_{m,j+1}^W$, is referred to as heat transfer across the wall. Most simulations of DWCs that have been described in the open literature neglect heat transfer across the wall [12]. There are two main reasons for this neglect: in part, it is because the inclusion of heat transfer is extremely difficult when using multi-column modular flowsheet simulations and, also, because heat transfer is not thought to be important in large DWCs. This contribution, however, can be very important in smaller columns often used in small scale experimental work.

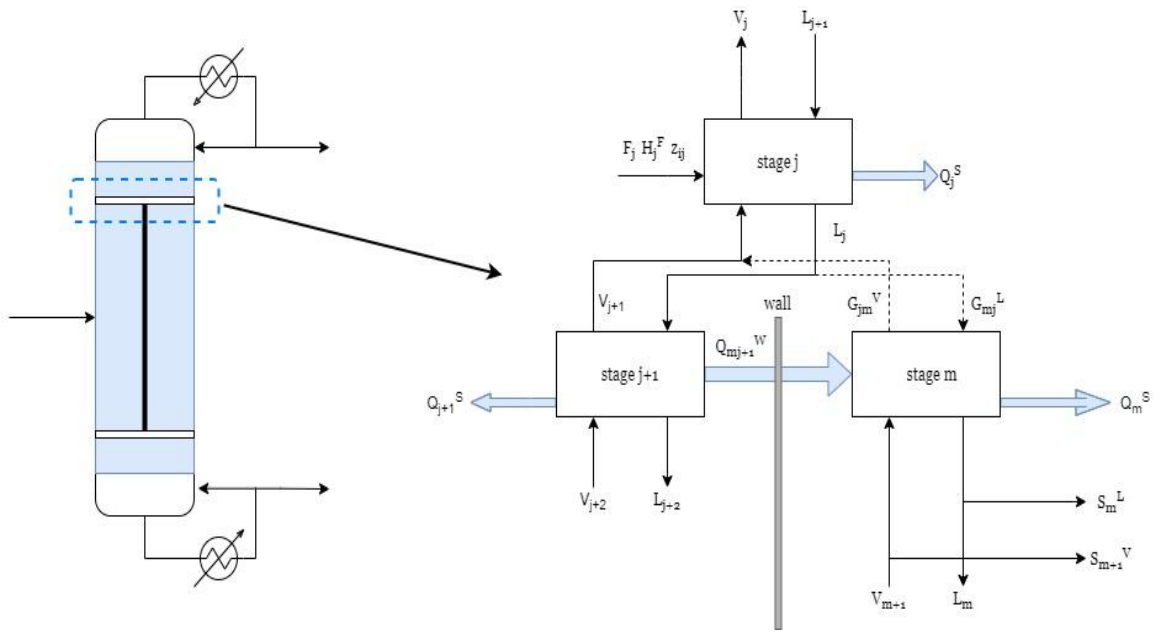


Figure 2. 9- Schematic diagram of sections in a DWC and corresponding equilibrium stage model [12]

CHAPTER 3

TOOLS AND INSTRUMENTS

Before starting to analyze the model of divided wall column with ABE mixture a presentation of tools and instruments used for this thesis work is worth to be done. In particular, the main tools and instruments used in this study are:

- SimCentral: commercial software for chemical plants simulation
- MATLAB ®: software of numerical computing environment

3.1 SimCentral

SimCentral is a new simulation platform developed by AVEVA. It is an innovative platform covering the entire process engineering lifecycle of design, simulation, and training to deliver the process side of the Digital Twin. Thanks to a simple graphical interface a complex industrial plant with a series of already implemented units operation can be simulated. The most important features of SimCentral are:

- Possibility of specifying any variable
- Undo changes
- Continuously solved with immediate feedback
- Snapshots of previous results

Moreover, it is also possible to change modes anytime and in any direction among flow-driven steady-state mode (Process), pressure-driven rating (Fluid flow) and Dynamics. In this thesis work, the steady-state mode is used to simulate the case study. For the complexity of the mixture, it was necessary to change the thermodynamic model started from the NRTL (Non-Random Two Liquids) model, which will be analyzed in the following paragraph.

3.1.1 Thermodynamic model

Starting from the Non-Random Two Liquids model for the ABE/W mixture it was necessary to change the binary interaction parameters of the component to have a most reliable thermodynamic model.

Component <i>i</i>	Component <i>j</i>	C_{ij}^o	C_{ji}^o	a_{ij}^o	C_{ij}^T	C_{ji}^T	a_{ij}^T
1-Butanol	Ethanol	1005.1	-717.72	0.29520	-	-	-
1-Butanol	Water	420.56	2622.7	0.42690	-	-	-
Acetone	Ethanol	36.297	434.82	0.29870	-	-	-
Acetone	Water	631.05	1197.4	0.53430	-	-	-
Ethanol	Water	-635.56	1616.8	0.14480	0.9907	2.0177	-

Table 3. 1- parameters of binary mixture for ABE/W mixture [49]

3.2 MATLAB ®

MATLAB, (MATrix LABoratory), is a multi-paradigm numerical computing environment developed by MathWorks along with its proprietary programming language. MATLAB® allows most of the calculus operations, such as matrix manipulations, plotting of functions and data, implementation of algorithms, ODE system solving, but the most interesting aspect is the ability to interface with programs written in other languages, including C, C++, Java, Fortran, Python. Main key features of this simulation software that justify its popularity are:

- High-level language;
- Simple environment tuned for iterative exploration, design, and problem-solving;
- Different graphics tools for visualizing data and custom plots;
- Several add-on tools to resolve specific problems like curve fitting, control system tuning, and many other tasks;
- The possibility to build applications with custom user interfaces;
- Interfaces to C/C++, Java®, .NET, Python, SQL, Hadoop, Microsoft Excel and, primarily, Aspen HYSYS;
- Royalty-free deployment options for sharing MATLAB programs with end-users.

CHAPTER 4
THERMODYNAMIC ANALYSIS OF
ABE/W MIXTURE

To introduce the optimal design and the flexibility analysis for the biorefinery case study, it is necessary to provide a study of the ABE/W mixture thermodynamics. This chapter will clarify the thermodynamic models applied, VLE equilibrium and graphic associated with the chemical mixture passing through the thermodynamics limits. Due to the feedstock composition fluctuations, especially in the bioindustries, it is very important to understand the areas highlighted above to have a robust model for the case study, particularly for the search of the flexibility index. In the industrial world, the ability to visualize the physical constraints of the separation process helps engineers to generate better design alternatives more quickly, resulting in significant time and cost savings.

4.1 RCMs overview

In distillation theory, the knowledge of thermodynamics of multicomponent mixtures is necessary. A widespread and well-established tool to assess whether a mixture can be separated by distillation is the use of Residue Curve Maps (RCMs) on phase diagrams, usually ternary or quaternary [49]. RCMs are scarcely used in chemical engineering; however, they are mathematically much easier to work compared to “stage-to-stage-column-composition profile” calculation. In other words, the residue curve map is a collection of liquid residue curves originating from different initial compositions. It contains the same information as phase diagrams but represented in a more useful way of understanding how to synthesize a distillation sequence. Similarly, for a distillation column equipped with trays, a distillation curve is defined as the locus of the tray compositions at total reflux. A distillation curve map (DCM) can be generated easily by choosing a

tray liquid composition [36]. From a geometrical point of view, RCM is the locus of the composition satisfying the equation:

$$\frac{\delta x_i}{\delta \tau} = x_i - y_i ; \text{ for } i = 1 \dots n \text{ (number of components)} \quad (4.1)$$

where x_i, y_i are the mole fractions of component i in the liquid and vapor phase, respectively, and τ is the nonlinear time scale. Each point of this line corresponds to a certain moment and a portion of evaporated liquid as well as to an equilibrium tray of an infinite distillation column. RCMs are convenient for the description of phase equilibrium because they are continuous and noncrossing. In order to clarify how to read a phase diagram when residue curve mapping is performed a few notation details by referring to Figure 4.2 will follow [49].

- Stable nodes (square): stationary points where all trajectories ultimately reach them, they correspond to the highest temperature points (heaviest component of a distillation bundle).
- Unstable nodes (circle): lowest stationary temperature nodes, all residue curves start from its and they correspond to the light component of a distillation bundle.
- Saddle: the points at which the trajectories approach from one direction and end in a different direction (as always is the point of an intermediate boiling component).
- Distillation boundaries, or separatrix line (black line): residue curves that divide the composition space into different

distillation regions, around these lines some points belong to different boundaries.

- Immiscibility region (green): the composition region where two liquid phases are present. The real compositions related to the aqueous and organic phase respectively are those at external points of the corresponding tie line.
- Univolatility lines (red): the points belonging to these lines satisfy the relation $\alpha_{ij} = \frac{K_i}{K_j} = 1$. Univolatility α -lines (also α -surfaces and hypersurfaces) divide the concentration simplex into regions of the order of components ($K_i > K_j > K_k$).

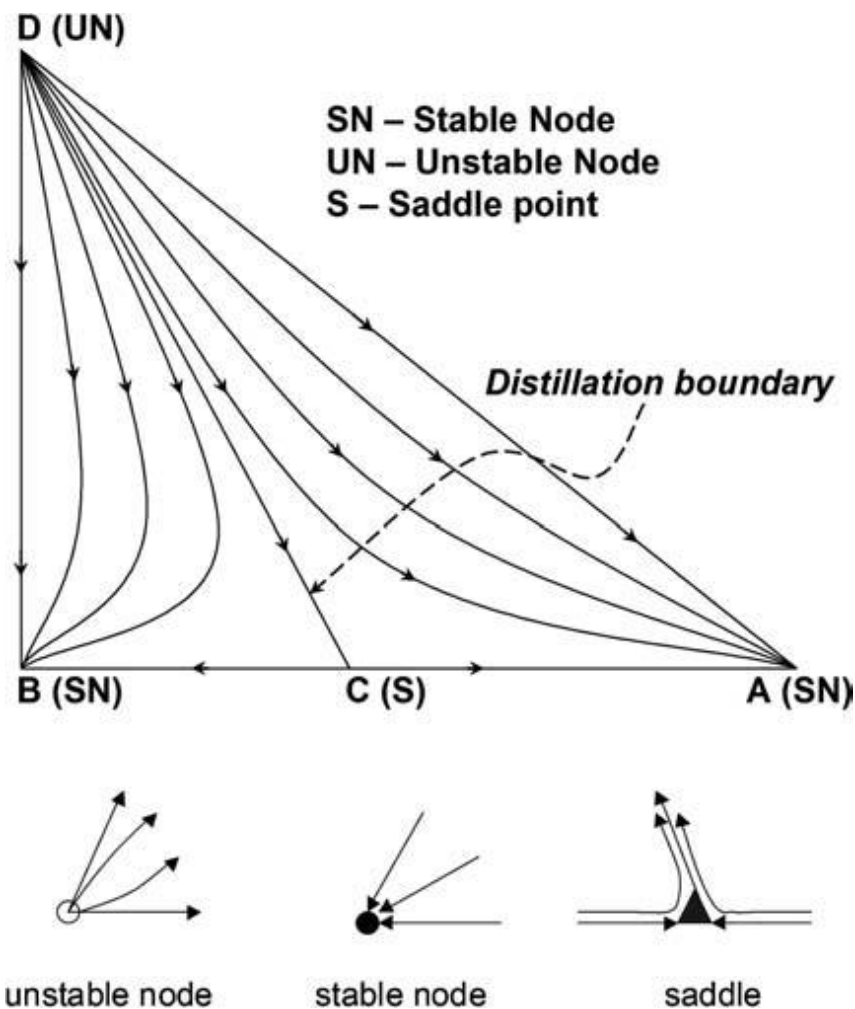


Figure 4. 1-Residue curve map (RCM) and types of characteristic points[37]

Points of pure components and azeotropes are stationary or singular points of residue curve bundles. At these points, the value $\frac{dx}{dt}$ in equation 4.1 becomes equal to zero. Temperature increases from an unstable node stable one, following the natural trend of the TNB of the compound in the mixture. A residue curves bundle is defined as a subregion with its stable and unstable points and differs from each other by initial or final points [37]. A characteristic feature of this zone is that in vicinity of its every point, no matter how small it is, points are belonging to two different bundles of residue curves. The concentration space for ideal mixtures is filled with one bundle of residue curves. Various types of azeotropic mixtures differ from each other by a set of stationary points of various types and by the various sequence of boiling temperatures in the stationary points. The distillation boundary can be a line, a surface or a hypersurface depending on the number of the compound in the mix; for a four components system become a surface. Separatrix lines are of critical importance to assess the distillation feasibility since they define at which side of the azeotropic composition the feed is located, i.e. the lightest and heaviest compounds that can be obtained by distillation for a given feed composition. Research studies [50] have also determined the relationship between the number of nodes (stable and unstable) and saddle points that can exist in a validly drawn RCM. The consistency of RCM with the azeotropic data can be verified by a theoretical test, expressed by the following relation based on topological arguments:

$$4 * (N_3 - S_3) + 2 * (N_2 - S_2) + (N_1 - S_1) = 1 \quad (4.2)$$

where N_i and S_i are the number of nodes and saddles, respectively, involving exactly i species from the ternary mixtures. Many different residue curve maps are possible when azeotropes are present. The thermodynamic ternary graphic below represent the behavior of the components for the mixture ABE/W. The temperature associated with each compound is the TNB.

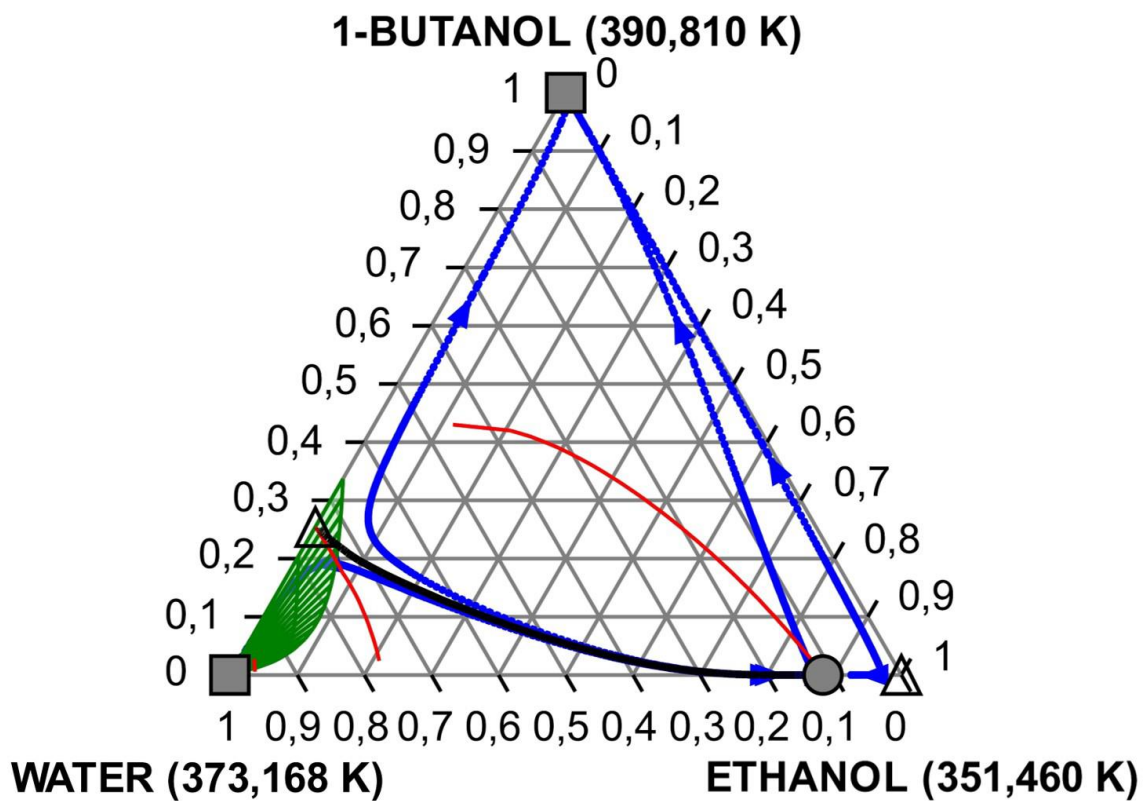


Figure 4. 2- RCM's on a ternary diagram [49]

In Figure 4.2 is possible to observe that:

- A liquid-liquid demixing in the green area.
- Heterogenous azeotropes, or eutectic point, at $x_{water}= 0.763$ represented by the empty triangle in the side water-butanol.
- Homogeneous azeotropes at $x_{water}= 0.11$ denoted by the full circle side water.

4.2 Thermodynamic model

Errico et al. [51] in this case study suggested the use of the Non-Random-Two-Liquids (NRTL) thermodynamic model for the mixture ABE\W. This model was chosen because it provided a good fit to experimental data for the most abundant alcohols in the feed mixture (ABE\W contains butanol and ethanol). Specifically, the binary vapor-liquid equilibrium (VLE) data of the methanol–isobutanol, ethanol–isobutanol, propanol–isobutanol, methanol–propanol, methanol–ethanol, ethanol– propanol pairs were validated against experimental data [52].

The activity coefficient for the species i in a mixture of n components is given by:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^n x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^n x_k \cdot G_{ki}} + \sum_{j=1}^n \frac{x_j \cdot G_{ij}}{\sum_{k=1}^n x_k \cdot G_{kj}} \cdot \left(\tau_{ij} - \frac{\sum_{m=1}^n x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^n x_k \cdot G_{kj}} \right) \quad (4.3)$$

where:

$$\ln(G_{ij}) = -a_{ij} \cdot \tau_{ij} \quad (4.4)$$

$$a_{ij} = a_{ij}^0 + a_{ij}^1 \cdot T \quad (4.5)$$

$$\tau_{ij} = \frac{\Delta g_{ij}}{R \cdot T} \quad (4.6)$$

$$\Delta g_{ij} = g_{ij} - g_{jj} = C_{ij}^0 + C_{ij}^1 \cdot T \quad (4.7)$$

The NRTL model requires three interaction parameters that are determined through the regression of experimental data for a specific system. In the process simulators used there wasn't any information for the coefficients for the organic binary mixtures (i.e. n-butanol-acetone, acetone-ethanol, n-butanol-ethanol). In order to have a robust thermodynamic model, a regression was used to adjust the missing parameters concerning experimental equilibrium data.

4.3 Thermodynamic feasibility assessment

In light of the above, the thermodynamic feasibility assessment is straightforward. The mixture under analysis shows two azeotropes, namely the water-butanol heterogeneous azeotrope and the water-ethanol homogeneous one. In the simulation case studies covered in the next chapters, the nominal feed composition and physical operative conditions are reported in Table 4.1 and Table 4.2. The molar fraction of the nominal conditions are far from azeotropic conditions, butanol is the most concentrated in the inlet mixture

Component	Molar fraction [-]	Mass fraction [-]	Flowrate [kmoll/h]
Acetone	0.134	0.123	43.309
Butanol	0.684	0.805	220.781
Ethanol	0.042	0.031	13.8191
Water	0.138	0.039	44.742

Table 4. 1-Nominal feed molar and massive compositions

Physical properties	Value	Units
Temperature	361.257	K
Pressure	101.325	kPa

Table 4. 2- Physical properties conditions

According to these properties, the composition profiles are always far from the homogeneous azeotrope; moreover, in the section where the butanol fraction is negligible the presence of acetone mitigates the non-ideal behavior of the remaining fraction. Due to the types of azeotrope and the “friendly behavior” of the acetone, the most critical operation is defined by the variation of the ratio butanol-water. This type of perturbation is the most likely to happen downstream wherein the fermenter this ratio changes with the seasonality of feedstocks. To better understand the distillation of the mixture in the DWC, in nominal and in perturbed conditions, it is useful to create a residue curve map. The starting point is writing the mass component balances for every species by the following method:

$$F * x_{iF} = D * x_{iD} + B * x_{ib} + M * x_{im} \quad (4.8)$$

with i is referred to the species acetone, ethanol, water and butanol. F , D , B , M are related to the four sections of the divided wall column, respectively feed, distillate, bottom, and mid-distillate.

The mathematical problem is solved thanks to:

- 2 recovery specifications for acetone and butanol in the distillation and bottom sections.
- 2 mass purity specifications for acetone and butanol in the distillation and the bottom section.
- ‘Key components’ hypothesis for ethanol and water respectively in the distillation and bottom sections.

Once this problem is solved, it is possible to represent the relative RCM's for the sections. Every graphical representation has 4 residue curves with four different colors:

- Green for the feed,
- red is for the distillate,
- blue is for the bottom,
- yellow is for the middle-distillate.

Figure 4.3 represents the quaternary and binary diagram for the nominal conditions. The four points (diamonds) identify the composition of mixture for each section. The characteristic of them is the coplanarity since they respect the same mass balances (see the light blue plane). Since the recovery ratio is fixed the lever rule resulting from mass balances can be applied to obtain the third point related to the distillate composition. It can be noticed that all these RCMs have the same stable and unstable nodes, which means separation by simple distillation is possible under nominal operating conditions. The yellow profile rises from the plane, descends and touches the other side of the azeotrope not passing through the node, which means unfeasible distillation.

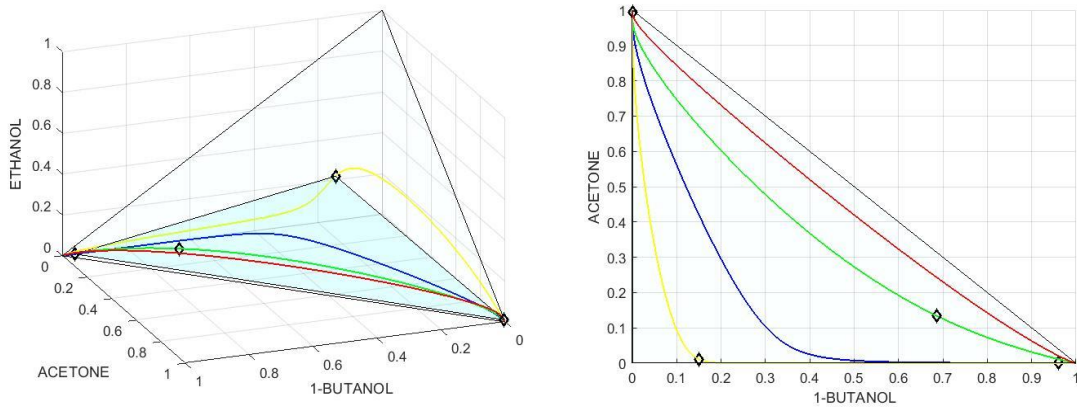


Figure 4. 3-Nominal operating conditions [49]

To assess the thermodynamic feasibility boundaries, the uncertain variables need to be perturbed. The most constraining variable is the water content in the feed stream, in particular, the distillation will be more critical, i.e. the butanol recovery at the desired purity to be more difficult, for a higher water fraction. The increase in water partial flowrate keeping unchanged the amount of the other components in the mixture can be represented on phase diagrams by moving the feed characteristic point along the line connecting the actual feed point and the pure water vertex. For an increase in the water content up to 11 % of the RCMs corresponding to distillate, feed and bottom still lie in the same distillation bundle as shown in Figure 4.4. The blue and yellow lines are much closer than before.

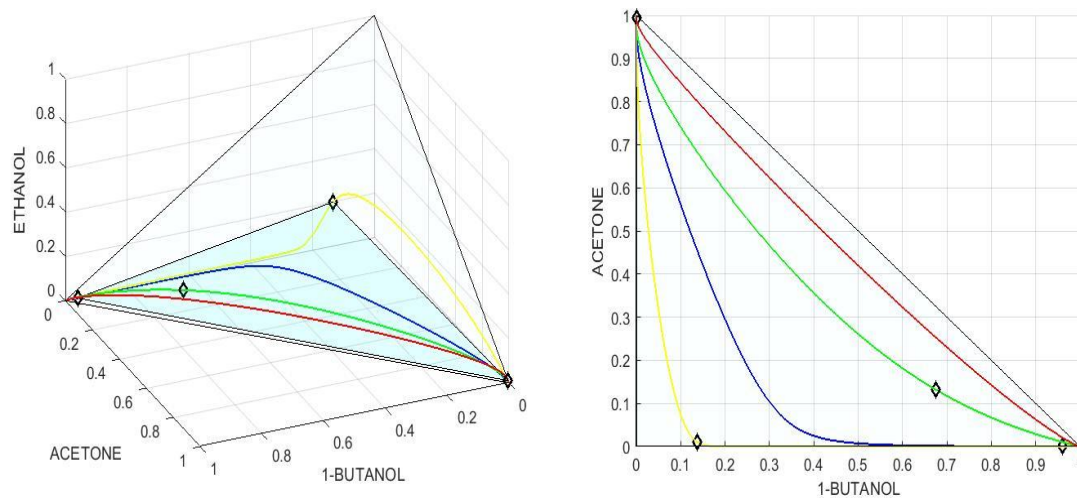


Figure 4. 4- Perturbed conditions [49]

When a deviation larger than 11% is applied, on the contrary, the stable node of the residue curve related to the intermediate withdrawal stream moves from pure butanol to pure water, i.e. it crosses a separatrix (cf. Figure 4.5). The separatrix crossing results in the impossibility of obtaining such a distillate from the given feed through distillation. The same analysis was carried out concerning each of the four components. As expected, the water molar fraction resulted to be the most constraining variable from a flexibility point of view than others. It can be then stated that the system thermodynamic flexibility limit is about 11%. This value represents the chemical-physical constraint to this operation whatever the affordable investment to design is the DWC. If higher flexibility is required, the only possible solution is to select a different separation process for such a mixture, like a train or mid-split configuration.

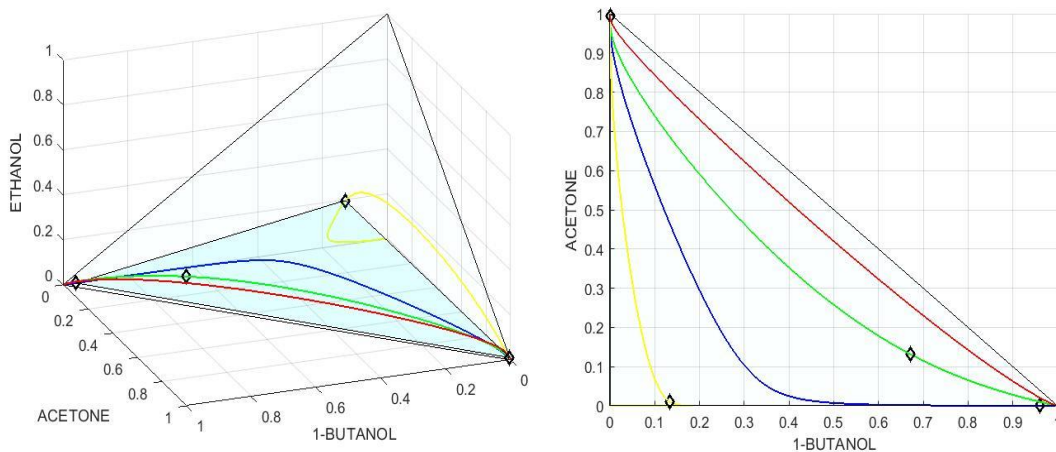


Figure 4. 5- Unfeasible distillation [49]

CHAPTER 5
PROCESS MODELING: ANALYSIS
OF SIMULATION LAYOUT AND
CASE STUDY

In this chapter the process modeling will be illustrated, the discussion will be divided into two principal paragraphs:

1. The overall layout of the ABE/W simulation with SimCentral software is illustrated in paragraph 1, in which all sections of the simulation are shown.
2. The case study has been analyzed and discussed with a description of models and tools.

5.1 SimCentral Layout

SimCentral platform is used to simulate the divided wall column with the ABE mixture for biobutanol production. As said in the previous chapters the DWC model is absent in SimCentral as in other simulators. Due to the lack of the divided wall column (DWC) model in SimCentral, the global process is divided into three parts:

- Thermal section, red zone in Figure 5.1, detailed in paragraph 5.1.1. It is composed of a heat exchanger to bring the mixture after the boiling point.
- Pre fractionator section, green zone in Figure 5.1, detailed in paragraph 5.1.2. it has the aim to make a first separation between the highest and heaviest components.
- Main column section, blue zone in Figure 5.1, detailed in paragraph 5.1.3. it is the equipment that completes the separation in which butanol to use as bio-combustible is obtained.

In Figure 5.1 the layout used in this thesis work is shown, the three sections mentioned above are highlighted by the three different colours. The need to

divide the DWC into two columns makes the numerical resolution of the column more complex for the software. These issues are mainly due to the interconnection between the two equipment which will be explained in the following parts.

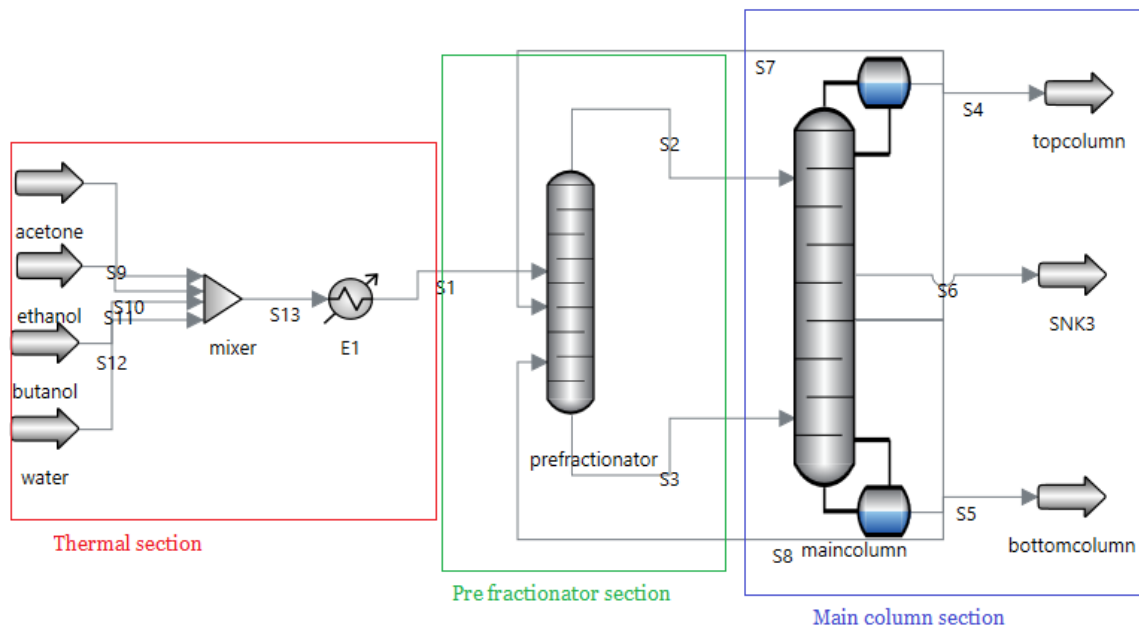


Figure 5. 1-Layout of a divided wall column in SimCentral software

5.1.1 Thermal section

In the configuration layout, it is possible to see the thermal section before the first column (pre-fractionator of the DWC). The thermal section is composed of a heat exchanger in which enters the entire feed of the process. In the real process, the ABE mixture isn't divided into four different streams as in the simulation but for help the calculation, in SimCentral acetone, butanol, ethanol, water arrive in a mixer from four different sources (cf. Figure 5.2).

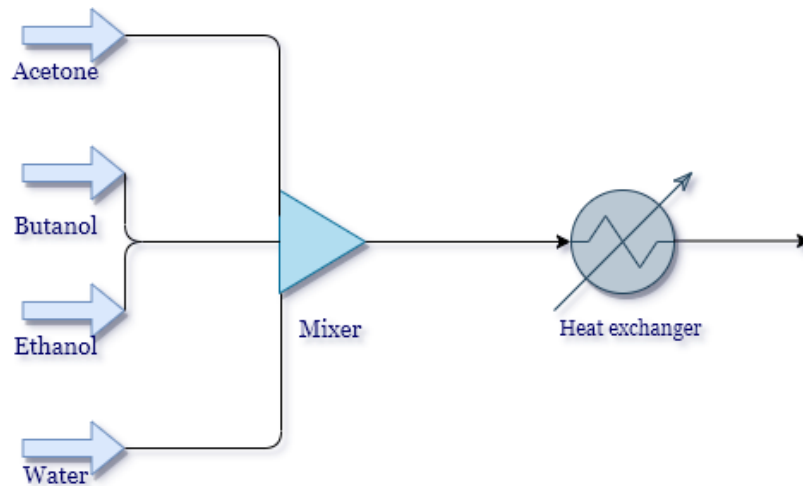


Figure 5. 2-Thermal section of SimCentral simulation

Its goal is to bring the mixture to the desired temperature of 361.257 K, starting from a temperature of 364.806 K after the mixer. The purpose of the thermal section is to bring the mixture before the bubble point of 361.66 before entering in the first column (cf. Figure 5.3). The only variable to control in the heat exchanger is the temperature because this unit has one degree of freedom, the other parameter of the heat exchanger can be seen in Table 5.1.

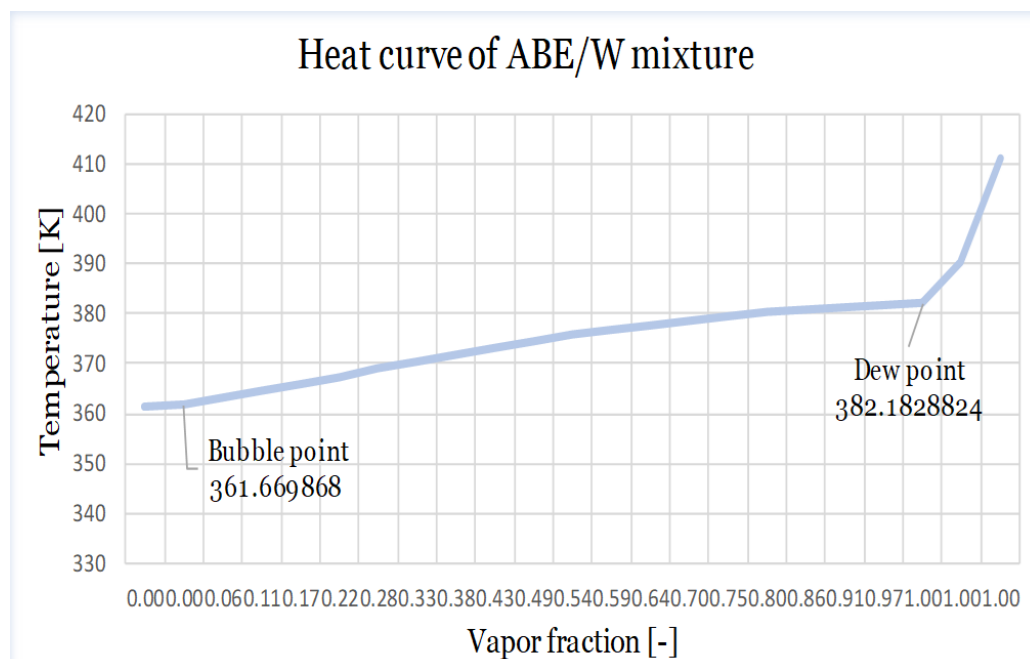


Figure 5. 3-Heat curve of the ABE/W mixture

Heat-exchanger parameters

Inlet temperature	364.806 K
Duty	-4.77 MW
Mass flow	5.64 kg/s
P_{in}/P_{out}	101.325 kPa

Table 5. 1-Heat exchanger parameters

5.1.2 Pre-fractionator section

The divided wall column is not present as a model in the SimCentral platform and some different equivalent models, as explained in chapter two, can be used to simulate this type of column. For this reason, in this study, it is simulated with two different columns. The first, the pre-fractionator, represents the left side of the DWC and it has the purpose of dividing the light component, acetone, in the top current of the column, from the heavy component, butanol, in the bottom of the column (cf. Figure 5.4). Usually, a DWC column works with three-component (A, B, C) and so the upper streams bring the total amount of light component A, with a little part of the medium one, B. The lower current instead brings the heavier component, C, with the rest of B. In this case, the total amount of acetone (A) is in the top streams

with water and ethanol, and the same occurs for butanol on the bottom of the column.

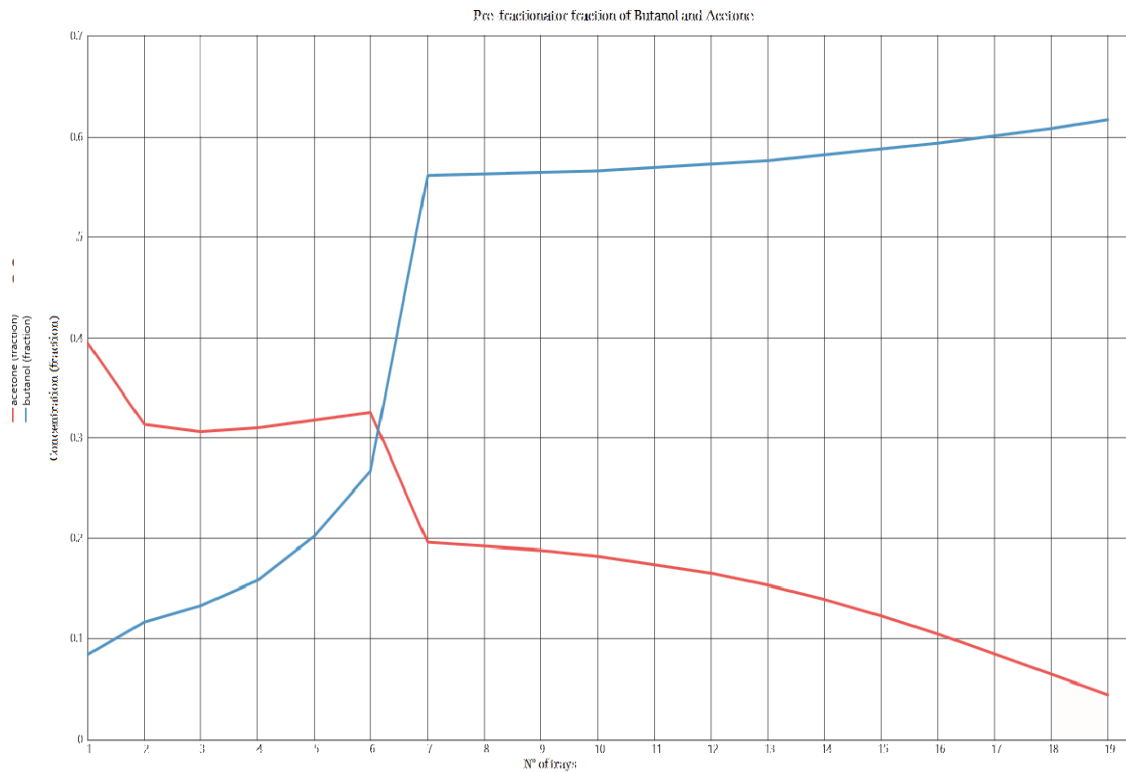


Figure 5. 4-Pre-fractionator profile fraction

The total feed of ABE/W enters the pre-fractionator after the mixer and the heat exchanger. Moreover, streams 7 and 8, enter respectively from the top and the bottom of the main column and enters in the pre-fractionator, it is possible to see the composition of these three streams in the next table (cf. Table 5.2). On the other hand, streams 2 and 3 exit respectively from the top and the bottom of the pre fractionator and enters in the main column (cf. Figure 5.5). In Table 5.3 the composition of the outlet streams is shown. It is possible to see that almost all acetone exits from the top of the column, and the butanol from the bottom. The value in Table 5.2 instead, shown that the streams exit from the main column have a more variable composition: if streams 7 has almost the total amount of acetone, stream 8 brings both butanol and water from the main column.

 Composition of the pre-fractionator inlet streams

Component	S1	S7	S8
Acetone	0.134	0.417	0.060
Butanol	0.685	0.015	0.341
Water	0.138	0.417	0.420
Ethanol	0.043	0.160	0.170

Table 5. 2-Composition of the pre-fractionator inlet streams

 Composition of the pre-fractionator outlet streams

Component	S2	S3
Acetone	0.484	0.020
Butanol	0.060	0.720
Water	0.382	0.180
Ethanol	0.074	0.080

Table 5. 3-Composition of the pre-fractionator outlet streams

These streams (2, 3, 7 and 8) characterize the integration of the divided wall column and thanks to them is possible to reach the aim of separate more than two-component with a single column. The height of the pre-fractionator, in this process simulation, corresponds to the height of the wall between the two different parts of the column. In a conventional distillation column, there are no interlinking streams, while in a DWC there are four interlinking streams that connect the two sides of the column. The design of the pre-fractionator will be discussed in the next chapter, to optimize the cost and emission of the total column. In Table 5.4 the structural characteristic of the column in optimal condition will be exposed. All the structural variables are known and are chosen to optimize the equipment. First the feed stage, for streams 1, 7, 8, change the final results in terms of duty of reboiler and condenser of the main column. Differently, all the process variables such as temperature and pressure, and the flowrate of these 4 streams (two, three, seven and eight) are obtained from the simulation.

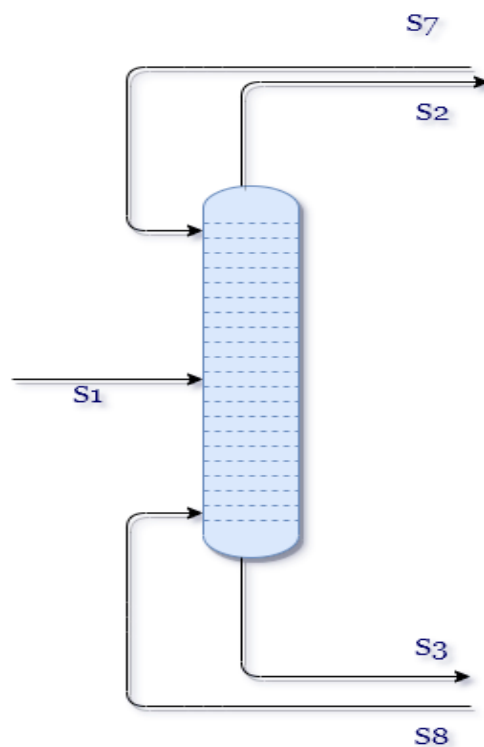


Figure 5. 5-Pre-fractionator section in SimCentral simulation

Pre-fractionator variables

Known variables	Unknown variables
Feed stage [S1] = 6	Pressure = 101.325 kPa
Feed Stage [S7] = 1	$T_{\text{top}}=350.787 \text{ K}$
Feed Stage [S8] = 19	$T_{\text{bottom}}= 367.981 \text{ K}$
Product Stage [S2] = 1	$F_{s2}=122.6 \text{ kmol/h}$
Product Stage [S3] = 19	$F_{s3}=358.253 \text{ kmol/h}$
Dcol =1.067 m	$F_{s7}= 45.58 \text{ kmol/h}$
The Hcol= 11.21 m	$F_{s8}=113.75 \text{ kmol/h}$
Hstage= 0.59 m	
Nstage=19	
$F_{s1}=322.651 \text{ kmol/h}$	

Table 5. 4-Variables of the pre-fractionator

In the next figure (cf. Figure 5.6) is possible to see the temperature profile of the pre-fractionator, as expected temperature rises from top to bottom of the column. Moreover, is possible to observe three different peaks in correspondence to trays immediately following those in which streams 1, 7 and 8 enter in the column. As far as concern pressure, this is constant in all columns and equal to atmospheric pressure. Another interesting profile is the vapor fraction ones in the column trays (cf. Figure 5.7):

- it is equal to 0.74 on the top of the column due to the big amount of acetone, the lighter element with lower boiling temperature (329 K), despite the temperature on this tray is the lowest of the column
- it is equal to 0.24 on the last tray for the contrary. Indeed, in this tray, there is a large amount of butanol, with a boiling temperature equal to 391 K and so despite the column temperature is equal to 367.981 the vapor fraction is the lowest.

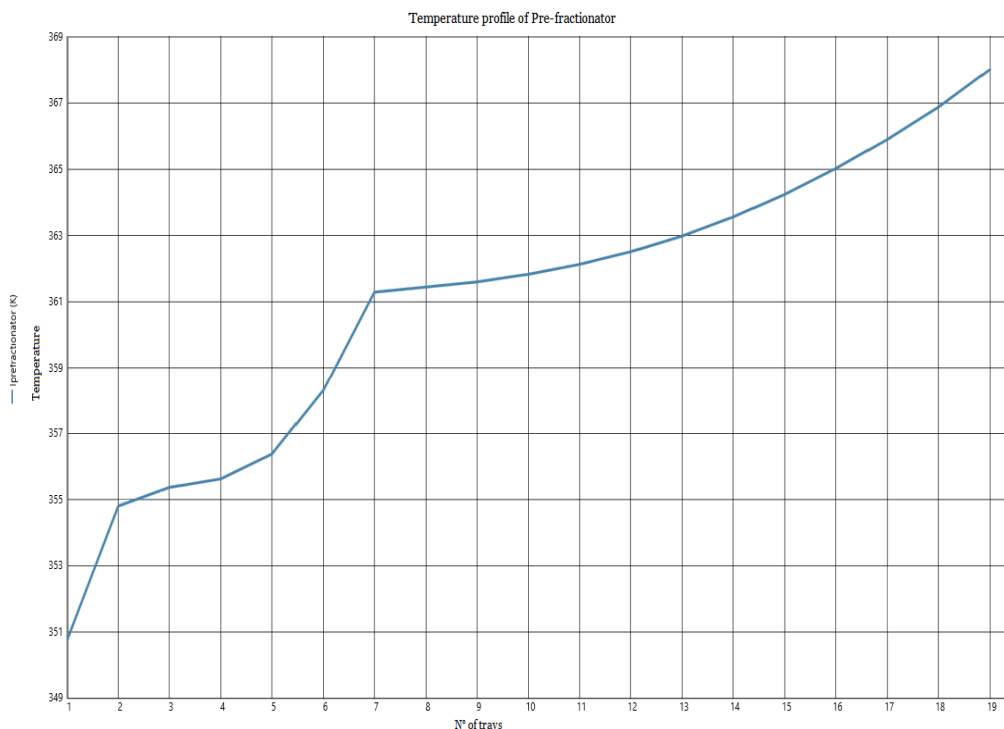


Figure 5. 6- pre-fractionator temperature profile

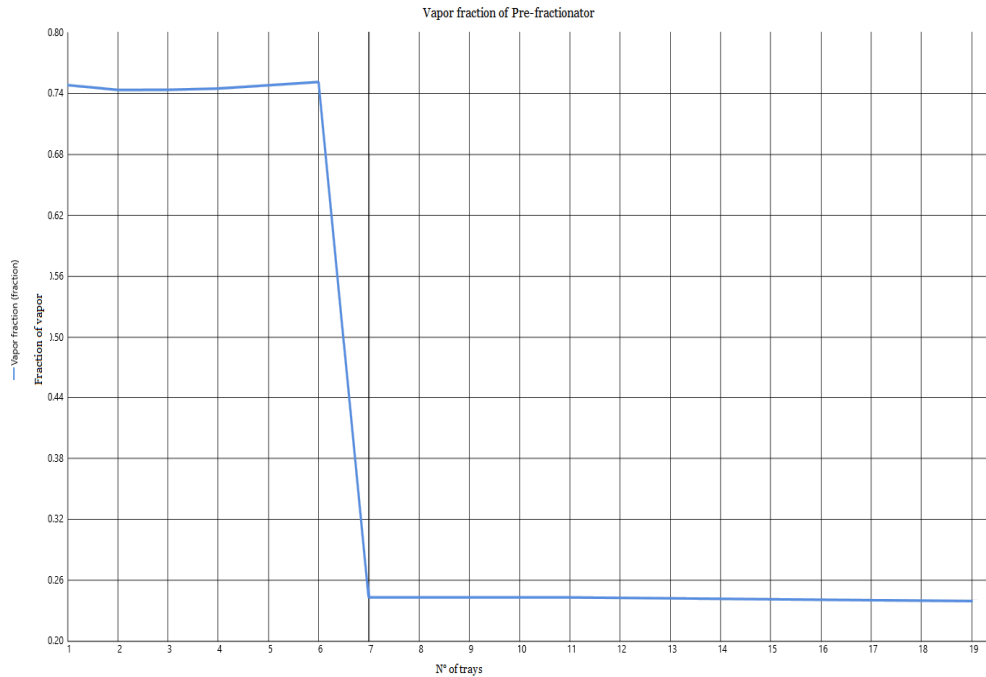


Figure 5.7- Vapor fraction of the pre-fractionator

5.1.3 Main column section

In this paragraph, the most important part of the column is analyzed. This is the part to the right of the wall. It is a distillation column with external reboiler and condenser. As a reboiler, a kettle reboiler with steam at 433.15 K is used, and for the condenser, a shell and tube exchanger with water at 298.15 K as cooling fluid is chosen. In this simulation, as said before, there isn't heat transfer across the wall. This choice is made for two different reasons:

- DWC is already difficult to simulate from a numerical point of view, and a heat transfer between the wall, that in simulation means between the two columns, would have helped make the simulation even more complicated.

- Heat transfer is a big contributor for a small column but since this column has 42 trays it is negligible. For these reasons, the only connections between the two columns are given by material streams and not heat streams, already analyzed for the pre-fractionator (cf. Figure 5.8).

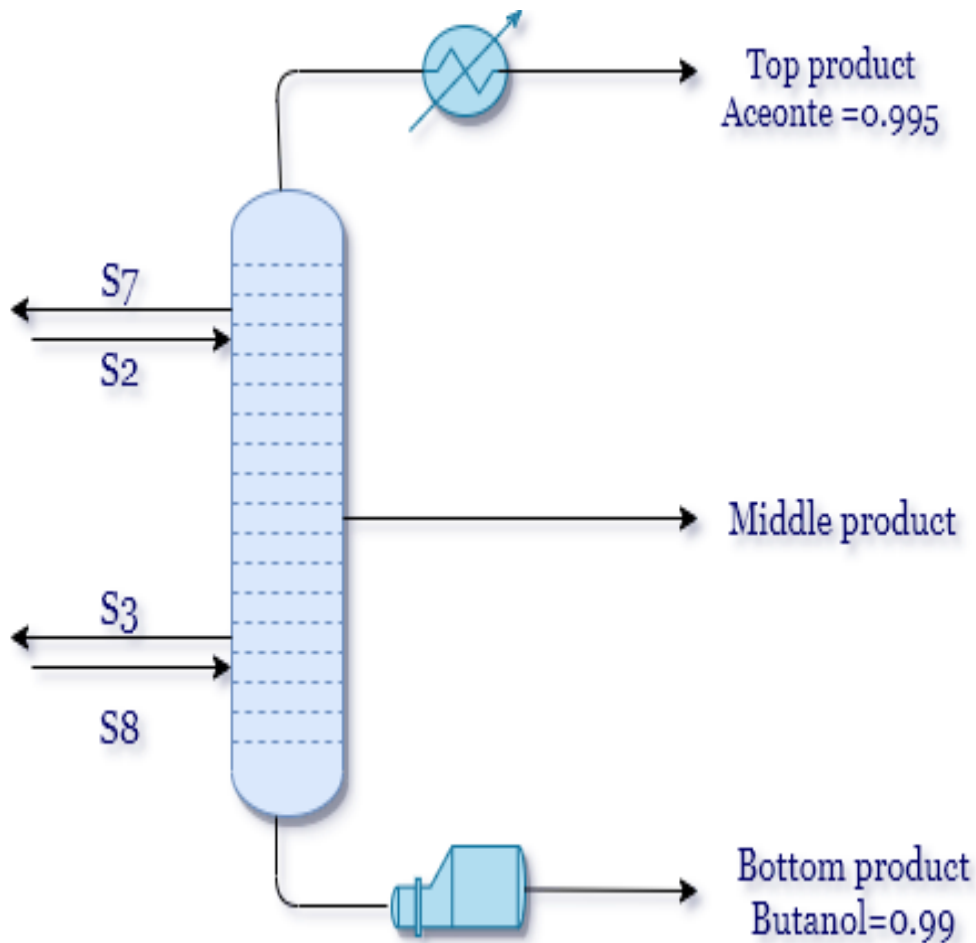


Figure 5. 8-Main distillation column section in SimCentral simulation

In Figure 5.8 is possible to see the connection between this column and the pre-fractionator, that are:

- Stream 2 exits from the top of the pre-fractionator and enters in tray 17 of the second column.

- Stream 3 exits from the bottom of the pre-fractionator and enters in the main column at tray 37.
- Stream 7 exits from tray 17 of the second column and enter on the top of the pre-fractionator.
- Streams 8 exits from tray 37 of the main column and enters on the bottom of the pre-fractionator.

The mass fractions of the previous streams are the same analyzed for the pre-fractionator in Table 5.2 and Table 5.3, so, the upper streams 2 and 7 are rich in acetone, the stream 3 is rich in butanol and stream 8 is rich in butanol and water. As far as concern the vapor fraction of these four streams:

- Streams 2 and 8 are saturated vapor
- Streams 3 and 7 are saturated liquid.

As done previously for the pre-fractionator, also, in this case, is necessary to analyze the known and unknown variable of this column. Also, in this case, the operative variables are unknown (reflux ratio, temperature along the column and pressure) and the structural parameter is known for the column design (cf. Table 5.5). The reflux ratio = 3.952 is a really important value for this simulation; this value indeed affects the duties of condenser and reboiler that for the huge cost of vapor, change the operating cost of the column. For this reason, in the optimization design, this value must be minimized to obtain the best configuration in terms of cost. The structure of the total DWC column follows the height of this column. Indeed, this column has 42 trays, while the pre-fractionator has only 18 trays, for this reason, the total vessel of this DWC column is referred to the sizes of the main column. In the optimization, as far as concern the structural cost (investment cost), also the number of trays of this column has been considered. The optimized column is the one chosen in all tables and figures of this chapter.

Known Variables	Unknown variables
Feed stage [S2] = 17	$T_{\text{top}} = 329.348 \text{ m}$
Feed stage [S3] = 37	$T_{\text{bottom}} = 387.446 \text{ m}$
Product stage [S7] = 17	$P_{\text{top}}/P_{\text{bottom}} = 101.325 \text{ kPa}$
Product stage [S8] = 37	$F_{s4} = 43.32 \text{ kmol/h}$
Product stage [S4] = 1	$F_{s5} = 212.038 \text{ kmol/h}$
Product stage [S5] = 42	$F_{s6} = 63.82 \text{ kmol/h}$
Product stage [S6] = 26	Reflux ratio = 3.952
$N_{\text{stage}} = 42$	Boilup ratio = 0.81
$D_{\text{col}} = 1.3 \text{ m}$	$Q_{\text{cond}} = -1.54 \cdot 10^6 \text{ kcal/h}$
$H_{\text{col}} = 24.78 \text{ m}$	$Q_{\text{reb}} = 1.84 \cdot 10^6 \text{ kcal/h}$
$H_{\text{stage}} = 0.59 \text{ m}$	
Efficiency = 1	

Table 5. 5-Known/Unkown variable of the main column

Now, is important to analyze also the three product streams of this column, which are the products of the entire DWC column. The column is divided into the rectifying section and stripping section, and the medium distillate divides the two different sections. In each section only the component with the extreme volatilities (heaviest or lightest) can be obtained with high purity; so, the rectifying section is used to obtained acetone with high purity, and the stripping section to obtain the heaviest component, butanol. In the next tables is possible to see the mass composition of these three product streams.

Component	S4	S6	S5
Acetone	0.995	0.018	0.000
Butanol	0.000	0.332	0.990
Ethanol	0.001	0.244	0.009
Water	0.004	0.406	0.001

Table 5. 6-Composition of the product streams

So, because on the top of the column there is mostly acetone in the vapor phase, the temperature is 329K, close to the TNB of acetone. On the other end, the bottom product is mostly composed of butanol with temperature, at the last tray of 387.446 K, really close to its TNB. The medium distillate is composed of water and ethanol, the molar fraction of the latter in the feed is very small, and so also in this current, there is a bigger quantity of water than ethanol. As said before the purpose of this column is to obtain pure acetone on the top and pure butanol on the bottom, there is no interest in the purity

of the third and fourth components (water and ethanol). The process could be more section to purify also water from the small amount of ethanol. But the purpose of this plant is to obtain biobutanol to use as biocombustible so it is useless to create a slower and complicate simulation. For these purpose is important to analyze the molar fraction profile of this column along with the trays, so it is possible to see that on the top a molar fraction of 0.995 of acetone is reached and on the bottom, a molar fraction of 0.99 of butanol is reached (cf. Figure 5.9).

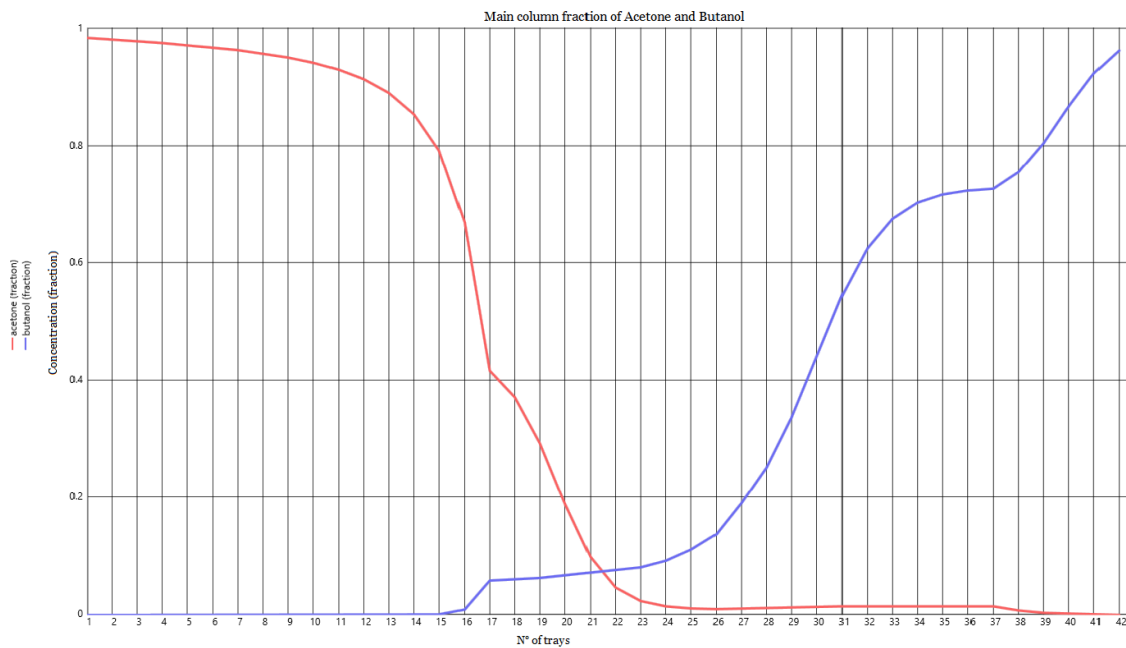


Figure 5. 9-Main column composition along with the tray of acetone and butanol

In the previous Figure 5.9, it is possible to see the acetone (red line) and butanol (blue) profiles along the column. The feed, rich in acetone, enters the column at tray 17, here it is possible to see a peak in the amount of acetone. On the other line, the feed rich in butanol enters tray 36 and, in this case, it is possible to see an increase of butanol amount until a molar fraction of 0.99 is reached on tray 42. In the next figure (cf. Figure 5.10) there is the profile of the other components, water (purple) and ethanol (green), in this graph is possible to observe that the big amount of these two elements is present in

the middle of the column, near the middle of the withdrawal column. The amount of water increases also near tray 17 because stream 2, that enters in this tray, contains prevalently acetone and water. Obviously, despite the peak of both the components the quantity of water and ethanol can't be compared. Indeed, feed is enriched in water (44.742 kmol/h) than in ethanol (13.8191 kmol/h). So, in stream 6 the flowrate of water correspond to 44.05 kmol/h and the flowrate of ethanol corresponds to 10.38 kmol/h.

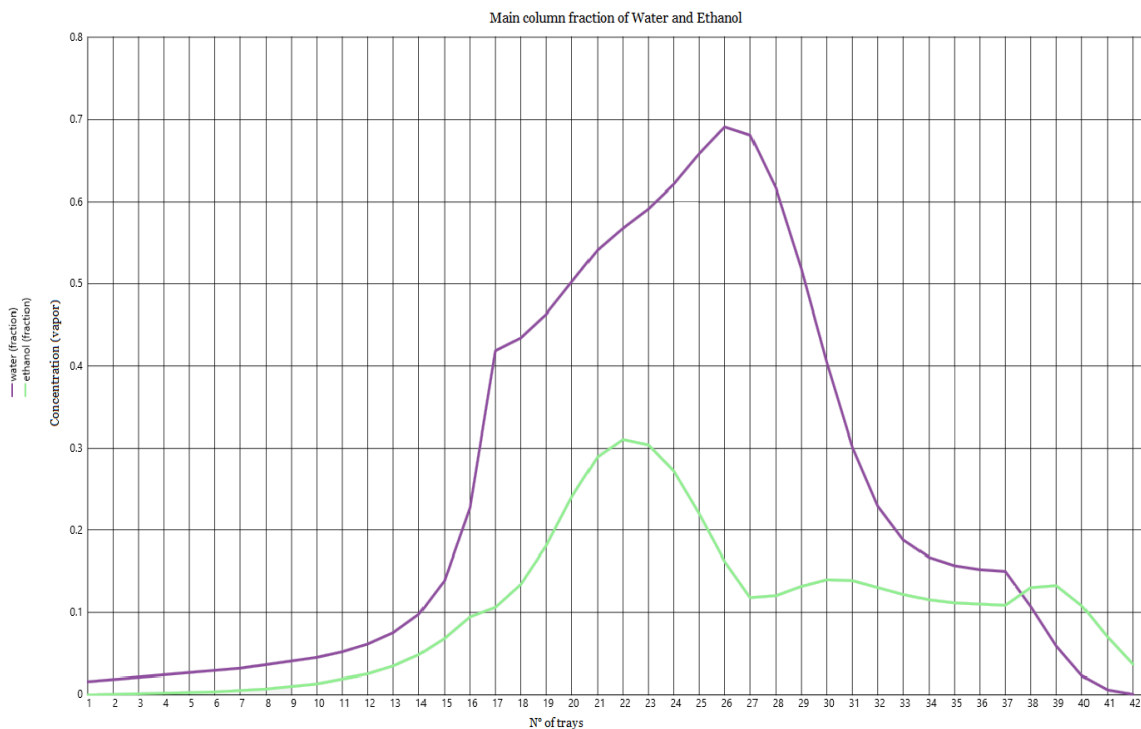


Figure 5. 10-Main column composition along with the trays of water and ethanol

Another important variable of the main column is temperature. In Figure 5.11 is possible to observe the temperature profile. The temperature starts at 329.34 K, which is close to the boiling temperature of acetone, and arrives at 387.44 K, close to the boiling temperature of the butanol. This is due to the composition of the flowrates in the top distillate, almost only acetone, and in the bottom one, only butanol.

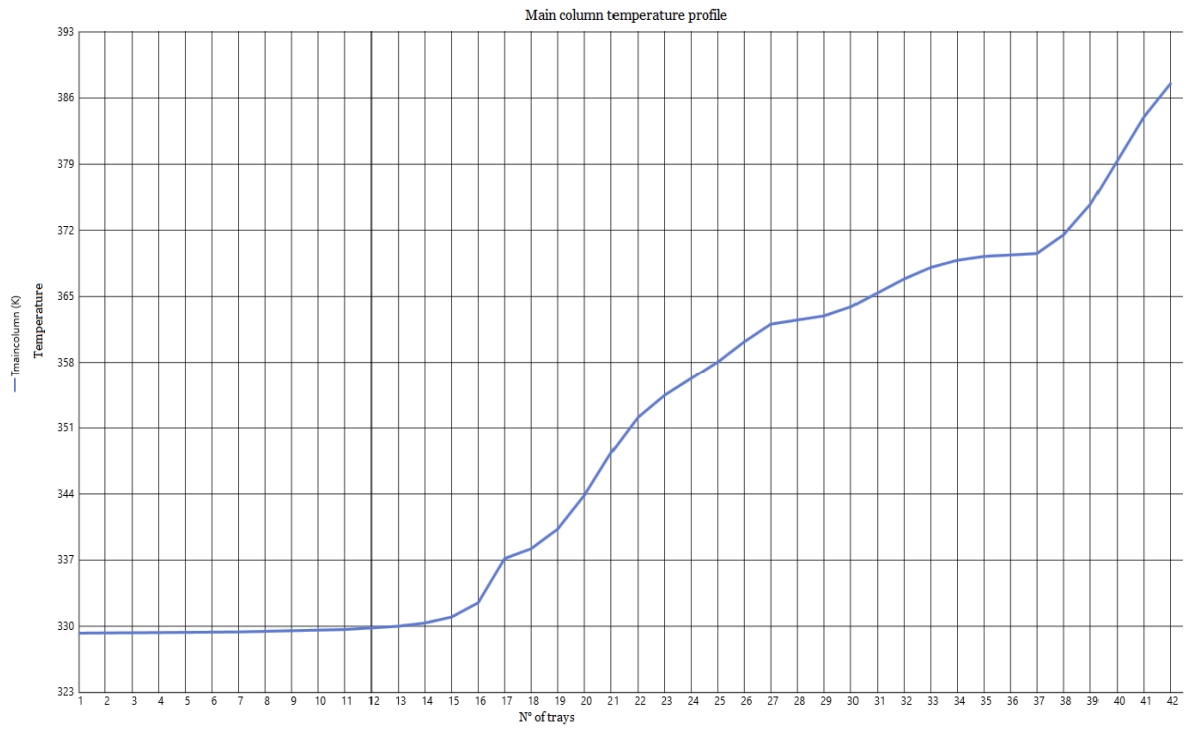


Figure 5. 11-Main column temperature profile

5.2 Case study

The main purposes of this study are two:

- To perform an economic assessment to identify the optimal DWC configuration for an ABE/W mixture separation;
- To perform a flexibility analysis under uncertain conditions with the same mixture.

With this aim, a case study referring to the separation of an ABE/W mixture has been outlined. The column studied in this thesis is in Figure 5.12.

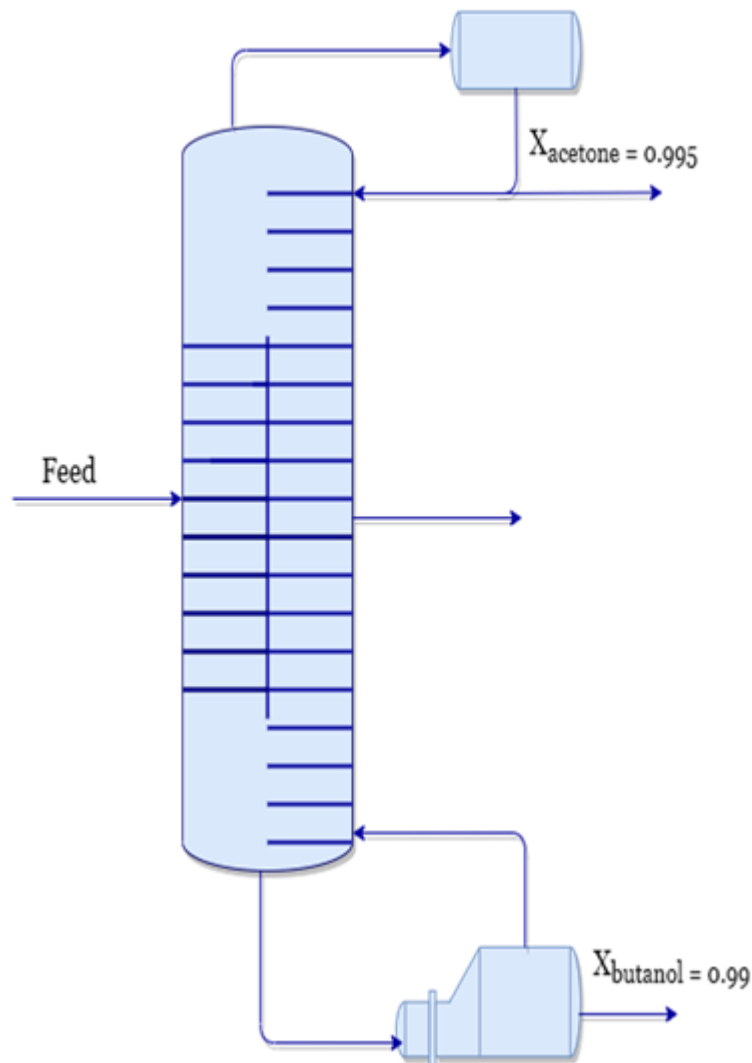


Figure 5. 12-Case study: Dwc for ABE/w separation

The nominal feed composition and flowrate of this case study are listed in Table 5.7.

Component	Molar fraction [-]	Mass fraction [-]	Flowrate [kmoll/h]
Acetone	0.134	0.123	43.309
Butanol	0.684	0.805	220.781
Ethanol	0.042	0.031	13.819
Water	0.138	0.039	44.742

Table 5. 7-Feed composition

In the next table (Table 5.8), is possible to see the physical properties of the mixture.

Physical properties	Value	Units
Temperature	361.257	K
Pressure	101.325	kPa

Table 5. 8-Table of physical properties

The successful recovery of biobutanol and acetone is the main aim of the profitability of the operation. Divided wall column configuration specifications are as follows:

- Mass fraction of acetone in distillate = 0.995
- Mass fraction of butanol in bottom = 0.99
- Recovery ratio of acetone = 0.985
- The recovery ratio of butanol = 0.964

The specifications are four in agreement with the study of the degrees of freedom of a divided wall column.

CHAPTER 6

**OPTIMIZATION OF THE DIVIDED
WALL COLUMN: COST
MINIMIZATION AND CO₂
EMISSION**

In this chapter, two principal aspects of this study will be discussed, to carry out the complete optimization of the case study column, under nominal conditions. The design obtained by the simulation may not be the optimum [53] and for this reason, is important to do an optimization. The optimal process is the one that allows reaching the specified separation [54], that in this case means to reach the top mass fraction of acetone equal to 0.995 and the bottom mass fraction of butanol equal to 0.99, at minimum cost and the minimum amount of emission. The optimal design of the DWC was performed by minimizing an objective function composed of:

- The total annualized cost (paragraph 6.1). To reach this value a complete economic analysis on capital cost and operating cost will be made. Different configurations of the same column with the same species will be analyzed to find them cheaper.
- The total annual emission of CO₂ (paragraph 6.2).

The coupling of these two different analyses will bring to the choice of the best configuration under the nominal condition. Finally, the comparison with an indirect design to obtain biobutanol was illustrated in paragraph 6.3.

6.1 Economic Assessment of Divided wall column in nominal condition

The term *economics* refers to the sum of capital cost, associated with the construction of the column and operating cost, associated with the operation of chemical processes. The total annualized costs are the index used in the objective function to consider the economy of the process. It is evaluated as the sum of the annualized capital cost and the operating cost ad reported in the equation:

$$TAC = \frac{\text{Capital cost}}{\text{project life}} + \text{Operating cost} \quad (6.1)$$

The system in analysis has nine structural variables:

- Location of the feed tray
- Location of the side stream trays
- Number of trays of the column and the pre-fractionator
- Location of the divided wall column
- Number of trays in divided wall column
- Reflux ratio
- Feed quality
- Liquid split ratio
- Vapor split ratio

And four process variables:

- Temperature
- Pressure
- Condenser duty
- Reboiler duty

These variables are used for the optimization of the product purities and the reboiler and condenser duty. As said in the study of the degrees of freedom of the column, the difference of pressure between the different sections of the DWC is equal to zero. An important variable to minimize in the optimization is the energy demands, as it accounts for the major fraction of the operating costs due principally to the steam, as well as the capital cost since the column diameter is a function of the internal vapor flow [54]. Now is important to describe in deep the method to calculate capital costs and operating costs.

6.1.1 Capital costs

The capital costs in this case study include the cost of the column, as far as concern shell and trays, kettle reboilers and shells and tube condenser [51]; each of these pieces of equipment has different parameters and rules to follow. It is possible to see in the previous equation (cf. equation 6.1), the capital cost is divided by the project lifetime that in this case is equal to ten years. It is important to remember that this is not a classical distillation column, for this type of calculus the only difference is the consideration of the wall: the total capital costs will be increased by 20% to take into account the cost of the wall [55]. As said before column capital cost is a function of diameter, which is a function of energy demand. Another important structural parameter for capital cost is the height of the column. It is known that an infinite column height is a prerequisite for minimum energy demand, therefore, minimizing the energy demand does not yield an optimal solution unless column height is fixed by additional constraints. To calculate the capital cost (CAPEX) of the process the different units must be studied separately, in this case they are:

- Column, that is composed of vessel and trays
- Condenser
- Reboiler

The formula used is the same for each component:

$$C_{BM} = C_p^0 * F_{BM} \quad (6.2)$$

$$\text{Log}_{10} * C_p^0 = K_1 + K_2 * \text{Log}(A) + [\text{Log}(A)]^2 \quad (6.3)$$

$$F_{BM} = B_1 + B_2 F_M F_P \quad (6.4)$$

A is the capacity or size parameter for the equipment.

K_1, K_2, K_3 are given parameter, with the minimum and maximum values of the capacity unity.

B_1, B_2 are constant.

C_{BM} is the bare module cost for each component and comprises direct and indirect costs. C_p^o is the purchased cost in base conditions: equipment made of most common material, as carbon steel and operate at near-ambient pressure. The value of C_p^o , as is clear by equation 6.3, depends on K_1, K_2, K_3 . These three constants can be used only in a range of value regard to the size parameter of equipment. If the size parameter is not respected the six-tenths rules is the way to calculated C_p^o following the equation 6.5:

$$\frac{C_A}{C_B} = \left(\frac{A_A}{A_B} \right)^{0.6} \quad (6.5)$$

“ a ” refers to equipment with the required attribute

“ b ” refers to equipment with the maximum size parameter

C in this study is to consider the C_p^o

A is the size parameter of the component

F_{BM} is the bare module cost factor, it depends on some items, plus the specific material of construction and specific pressure of the system. F_p , in equation 6.4, indicates the pressure factor and follows equation 6.6, in this work the pressure is equal to 1, so the pressure factor can be not considered and F_p is considered equal to one.

$$\text{Log}_{10} F_P = C_1 + C_2 \text{Log}_{10} P + C_3 [\text{Log}_{10}(P)]^2 \quad (6.6)$$

with C_1, C_2, C_3 constant equal to 0.

F_M always in equation 6.4 is the material factor and in this analysis is equal to 1. The last consideration, before starting with the analysis of the various component, is about the inflation index used to evaluate the cost. The most common indexes are the M&S (Marshall and Swift) and the CEPCI (Chemical Engineering Plant Cost Index). In this study, the first is used and is multiply for the C_p^o , for each component. The M&S index for 2018 is 1638.2 and it must be divided for M&S of 2001 equal to 1100 obtaining a value of 1.476. In the Table 6.1 the index for the column CAPEX is shown. In Table 6.2 the Capital cost of different configurations is analyzed. It is possible to see that column with trays from 37 to 52 is studied. These different configurations first were optimized changing feed tray, reflux ratio and diameter. As far as concern the latter, both pre-fractionator and main column diameter as to be taken into account for the total column diameter:

$$A_{DWC} = A_1 + A_2 \quad (6.7)$$

$$D_{DWC} = \sqrt{\frac{4A_{DWC}}{\pi}} \quad (6.8)$$

Instead of for the height, only the main column trays are considered for the vessel, plus a constant of 4.6 m for the basement of the column. The value in Table 6.2 corresponds to the optimal column design for all configurations. Since the capital cost depends only on the structural variables, as diameter, height, area, and volume, there is no difference in C_p^o and C_{BM} between the optimized and non-optimized column configuration. Differently, when the Operating Cost will be calculated, the optimization of each column will be important for the choice of the best column. All the Indexes for the CAPEX reported in the next tables come from Turton, “Analysis, Synthesis, and Design of chemical process” [56].

Table of Indexes for column

C_P°column	
K_1	3.4974
K_2	0.4485
K_3	0.1074
$C_{BM} \text{ column} = C_P^{\circ} \text{column} * F_{BM}$	
F_{BM}	4.07
C_P° Trays	
K_1	2.9949
K_2	0.4465
K_3	0.3965

Table 6. 1-Index for Column CAPEX [56]

Column Capital Cost

Plant life	10	10	10	10	10	10	10	10	10	10
Trays	37	39	40	41	42	43	44	45	48	52
Feed tray	7	7	7	7	7	8	8	8	8	8
H[m]	26.545	27.764	28.374	28.984	29.593	30.203	30.812	31.422	33.251	35.689
D[m]	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69
Area[m²]	2.243	2.243	2.243	2.243	2.243	2.243	2.243	2.243	2.243	2.243
Volume[m³]	59.54	62.28	63.64	65.01	66.38	67.75	69.11	70.48	74.58	80.06
c_p°trays[\$]	84277	88959	91300	93641	95982	98323	100664	103055	110028	119393
c_p°col [\$]	63216	65622	66823	68022	69221	70418	71613	72808	76387	81146
C_{BM}°[\$]	341569	356043	363272	370494	377712	384925	392133	399337	420924	449658

Table 6. 2-Capital cost of Column, for different configuration

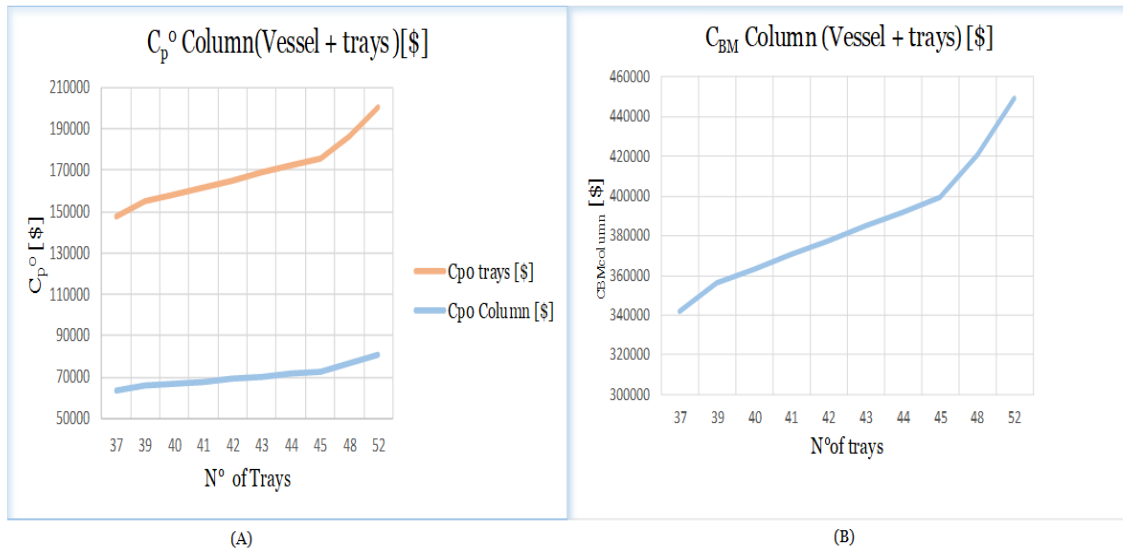


Figure 6. 1- (A) C_p^o column (Blueline) and Trays (Redline), (B) C_{BM} column (Vessel + Trays) [\$]

In Figure 6.1 (A) and (B), capital cost trends of vessel and trays are shown. The first figure represents the value of C_p^o for each component of the column, is clear that the red line, trays C_p^o , has a bigger value than the blue line. Indeed, the weight of the C_p^o of the trays in total capital cost is greater than that of C_p^o of the vessel. The trends of these two lines are similar and follow also the C_{BM} of the total column. Figure 6.2 shows that the column with the lower capital cost is the little ones, which is the 37 trays ones. This type of cost is linked only with structural variables and so is obviously that the small column is cheaper than the other in terms of Capital cost. To build a little column, with fewer trays and a little vessel, there is a need for fewer materials, but probably this column will need more duty at condenser and reboiler. Now, the Condenser and Reboiler capital cost will be studied. In the next table (Table 6.3) the indexes of the condenser are shown. They are referred to as a shell and tube heat exchanger, which is the type of equipment chosen for the condenser. Also, in this case, as well as for the column F_P and F_M are set equal to one.

Table of Index for condenser CAPEX

C_P⁰ condenser	
K₁	4.3247
K₂	0.303
K₃	0.1643
C_{BM}=C_P⁰ condenser*F_{BM}	
B₁	1.63
B₂	1.66
F_P	1
F_M	1

Table 6. 3-Index for condenser CAPEX [56]

Condenser Capital Cost

Trays	37	39	40	41	42	43	44	45	48	52
Q_{con}[kcal/h] *10⁶	1.60	1.58	1.56	1.55	1.546	1.542	1.542	1.541	1.541	1.540
T_{top}[K]	329.35	329.35	329.34	329.34	329.34	329.34	329.34	329.34	329.34	329.34
T_w [K]	298.15	298.15	295.15	298.15	298.15	298.15	298.15	298.15	298.15	298.15
U[W/m²/K]	470	470	470	470	470	470	470	470	470	470
Area[m²]	126.86	125.28	123.70	122.91	122.62	122.28	122.28	122.19	122.19	122.14
c_p^ocon [\$]	37963	37781	37598	37507	37473	37433	37433	37423	37423	37418
C_{BM}^o[\$]	124899	124300	123699	123398	123286	123156	123156	123124	123124	123106

Table 6. 4-Condenser capital cost [56]

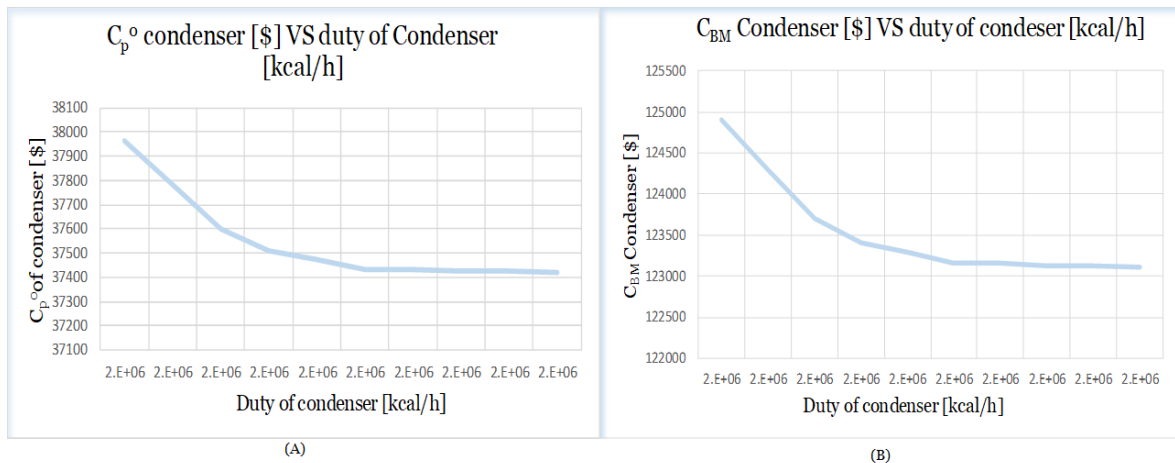


Figure 6. 2-(A) C_p^o condenser in the function of duty of condenser [kcal/h], (B) C_{BM} condenser in function of duty of condenser [kcal/h]

In Figures 6.2 (A) and (B), the trends of C_p^o and C_{BM} of the condenser, in function of duty of equipment, are shown. These two figures have the same profiles: the capital cost decrease with the decrease of condenser duty, which means that is a decrease with increasing of trays number. This is contrary to the previous trends, if the CAPEX of the column increases with the number of trays, the CAPEX of the condenser decreases with these. The reason is that these two C_{BM} depend on different variables: while the first depends on the structural variables, like the height, the second depends on the duty of the condenser. Thanks to the higher number of trays and the smaller reflux ratio, the bigger column has a smaller condenser duty. As far as concern the reboiler, it is chosen to consider a Kettle reboiler, and in the next table (cf. Table 6.5) all the index of this component is present. The size parameter of the Kettle reboilers for the C_p^o calculation is the area, and the maximum value is 100 m², the area of the heat-exchanger in this study is greater than 100 m², so the rules of six rules must be used, the data is in Table 6.5. Another difference of reboiler respect to other equipment is the term refers to the pressure, in fact, the pressure of reboiler in set to 4 bar, so F_p is different to one and it is calculated with equation 6.6.

Table of the index for Reboiler CAPEX

Six/Tenths rules	
$A[m^2]$	100
$C_{p^0 reb100m2}$	144639.315
$C_{BM} = C_{p^0 Reboiler} * F_{BM}$	
B_1	1.63
B_2	1.66
F_M	1
C_1	0.03881
C_2	0.11272
C_3	0.08183

Table 6. 5-Table of the index for reboiler CAPEX [56]

Reboiler Capital Cost

Trays	37	39	40	41	42	43	44	45	48	52
Qreb[kcal/h] *10⁶	1.90	1.88	1.86	1.857	1.849	1.846	1.845	1.845	1.844	1.843
Tbot[K]	386.33	386.69	386.96	387.18	387.44	387.50	387.60	387.68	387.76	387.77
Tvap[K]	415.70	415.70	415.70	415.70	415.70	415.70	415.70	415.70	415.70	415.70
U[W/m2/K]	550	550	550	550	550	550	550	550	550	550
Area[m2]	136.74	136.98	137.20	137.63	138.31	138.40	138.85	139.21	139.53	139.47
$c_{p^0 con}$ [\$]	174514	174697	174863	175197	175717	175782	176126	176401	176642	176600
C_{BM^0} [\$]	576647	577253	577801	578903	580623	580837	581975	582881	583680	583540

Table 6.6-Reboiler Capital Cost

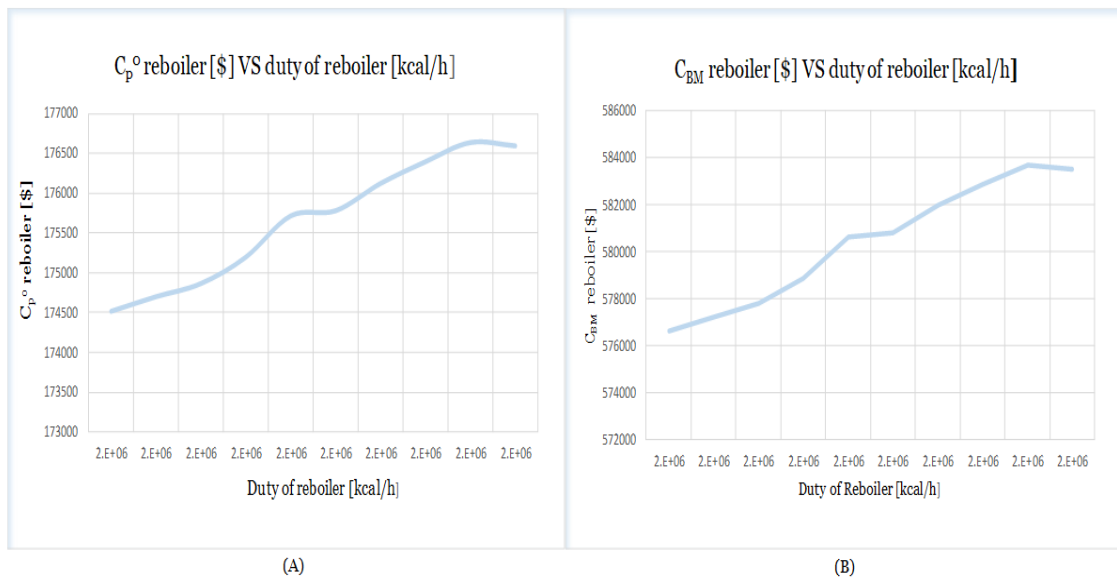


Figure 6. 3- (A) C_p^o of reboiler [\$] VS duty of reboiler [kcal/h], (B) C_{BM} of reboiler [\$] VS duty of reboiler [kcal/h]

In Figures 6.3 (A) and (B) the trends of C_p^o and C_{BM} of the reboiler are shown. As in the previous case the reboiler duty decrease increasing the number of trays. Differently from the capital cost of condenser, in this case, is possible to say the opposite trend. This is due to the variation of dT ($T_{vapor}-T_{bottom}$) between the configuration: if in the case of condenser dT ($T_{water}-T_{top}$) used to calculate Q is almost constant, in this case, it decreases leading to an increase in the cost of a piece of equipment. In these graphs, having used the six/tenths rules the trend are approximate respect the precision of the precedent analysis. As a result of all these calculations, the total capital cost of the process is obtained. Among the three factors, the one with the greatest weight is the third one, so the investment cost for the reboiler is bigger than that for condenser and column. However, the value for the reboiler production are all similar and they don't affect the total trends. So, as is possible to see in Figure 6.4, the trend of the CAPEX of the total process follows the trends of the CAPEX of the column. In conclusion, the first analysis highlight that the column with 37 trays is the cheaper one (cf. Figure 6.4).

Total CAPEX of the process

[\$]	1251739	1269116	1277726	1287355	1297947	1306702	1316718	1326412	1353274	1487565
[\$/year]	125173	126911	127772	128735	129794	130670	131671	132641	135327	138756

Table 6. 7-Total CAPEX of the process in \$/year

In Table 6.7, the cost per year is shown. These values are obtained following equation 6.1: the three different contributes of the column, condenser and reboiler are divided for the plant life, set equal to 10 years. At least, these values (cost in \$/year) are shown in Figure 6.5.

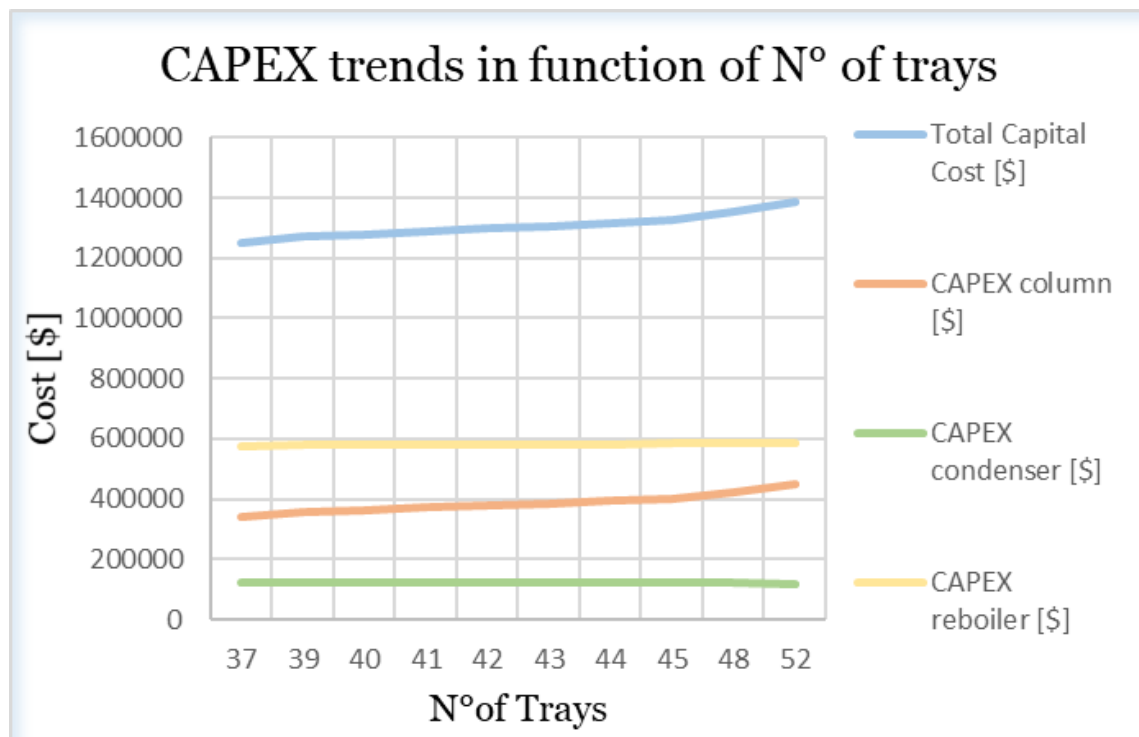


Figure 6. 4-CAPEX trends in the function of N° of trays

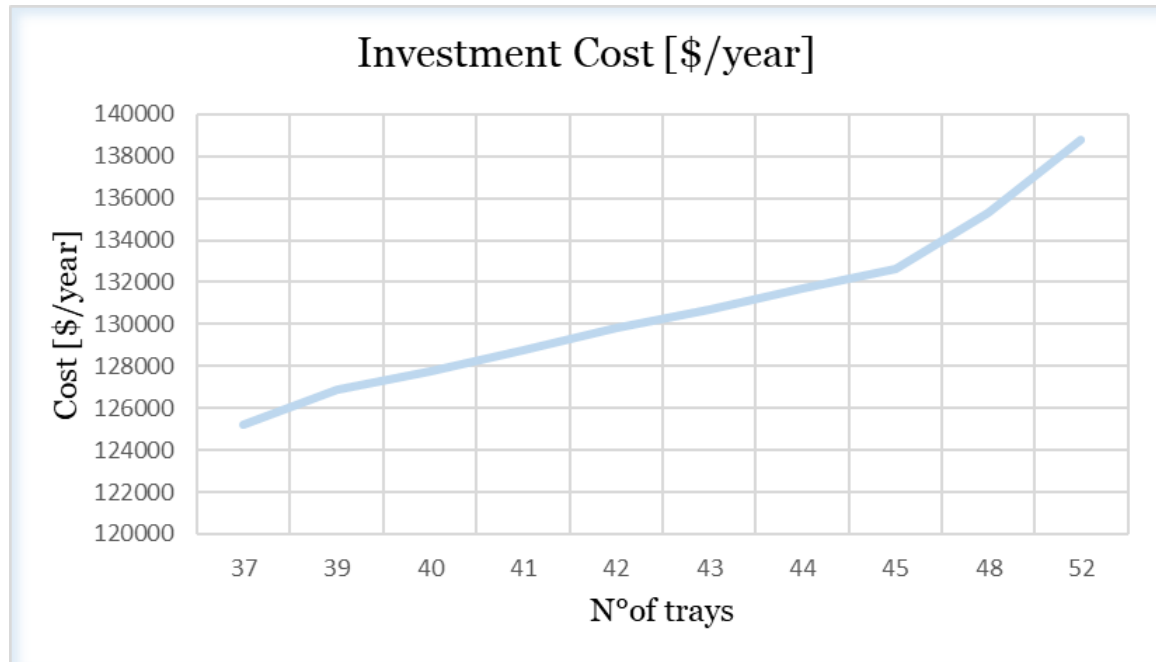


Figure 6. 5-Investment Cost [\$ /year]

6.1.2 Operating cost

The operating cost reflects how much money it takes to operate a chemical process. The operating cost (OPEX) is obtained as the sum of the costs associated with the auxiliary fluids for the reboiler and condenser. There is no column contribution to this type of cost. The equation to find OPEX is simpler respect to the method to find CAPEX and follow equation 6.9:

$$OPEX = Cost_{utility} [$/GJ] * Q_{reboiler/condenser} [GJ/year] \quad (6.9)$$

In the next table (cf. Table 6.8) the utilities that would likely be provided to condenser and reboiler are shown.

Utilities to provide to equipment

Condenser	Water at 1 bar From 30° to 45°	0.354 \$/GJ
Reboiler	Steam at 4 bar	7.78 \$/GJ

Table 6. 8- Utilities to provide equipment [56]

The whole column configuration analyzed also for the case of CAPEX, was optimized to reach the lower reflux ratio and so the lower duty at condenser and reboiler; the result will be seen in Table 6.9.

Total OPEX of the process [\$/year]

C_w	19323	19081	18840	18719	18674	18622	18622	18609	18609	18602
C_s	504301	498992	495011	492888	490764	490127	489968	489703	489437	489172
OPEX	523624	518074	513851	511607	509439	508750	508591	508312	508047	507774

Table 6. 9-Total OPEX of the process

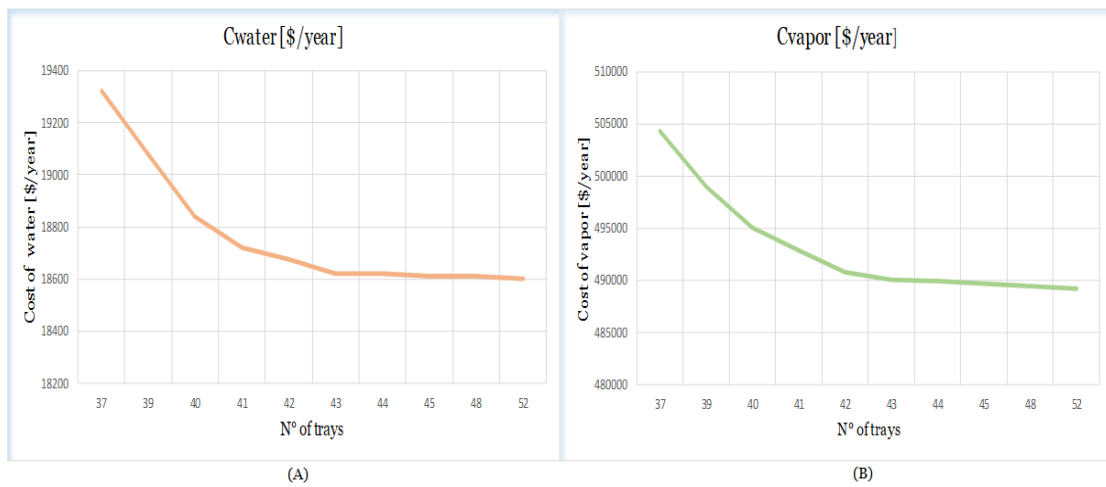


Figure 6. 6-(A) Cost of water to provide at the condenser in \$/year, (B) Cost of vapor to provide at the reboiler in \$/year

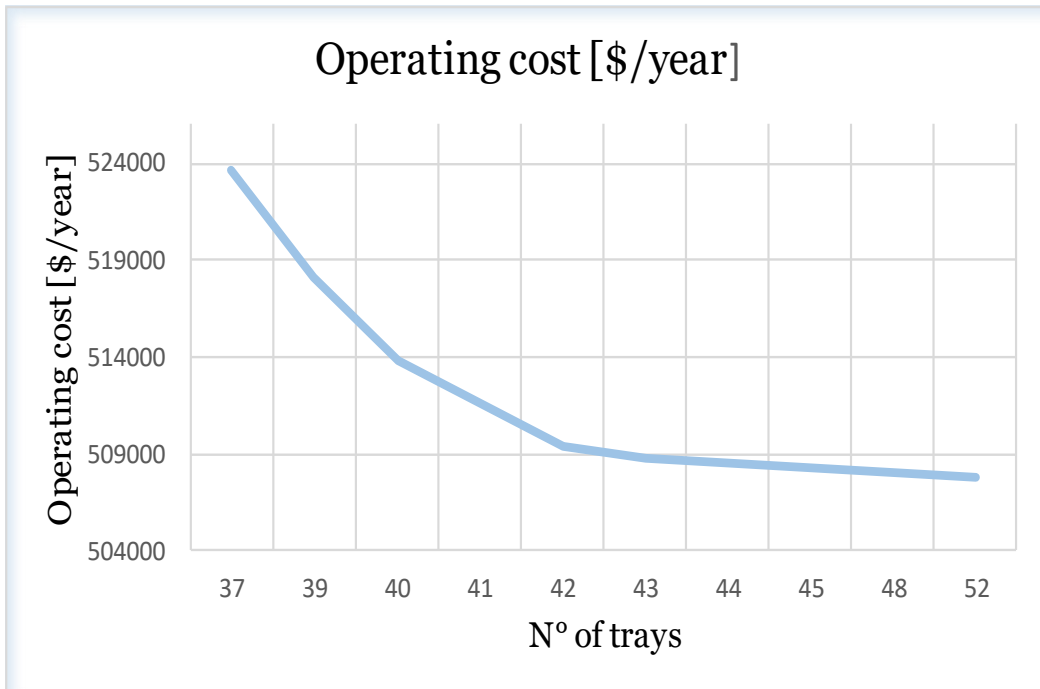


Figure 6. 7-Total Operating cost (reboiler + condenser) of the process \$/year

In Figures 6.6 (A) and (B) and 6.7 the operating cost for condenser, reboiler, and the total process are shown. These three figures have the same trends: cost decrease with increasing the number of trays. This means, as said before, that the increase of several trays corresponds to reboiler and condenser duty decreasing. The curve mainly decreases in the first part, in correspondence with configuration with fewer trays. After the column with 42 trays, the decrease is very small because the duty and reflux ratio remain also constant. Moreover, Figure 6.6 shows that the contribution of the condenser duty is less than the reboiler one; this is due to the cost of the utilities: the water at 298.15 K and 1 bar has lower price respect to steam at 415.15 K and 4 bar. As is possible to see from the previous number the most important values for the TAC of DWC are the OPEX. Considering the entire configuration, DWC allows us to have lower OPEX respect to the classical configuration (with two or three different columns), but the values of duty of reboiler and condenser are higher, considering every single component, in this case.

6.1.3 Total Cost

As far as concern the total Cost, it is due to the sum of CAPEX and OPEX following equation 6.1. The value of the Total cost in \$/year is shown in Table 6.10, and it is shown as the following figure (cf. Figure 6.8) that the cheaper configuration is the 42 trays one.

The total cost of the process \$/year

37	39	40	41	42	43	44	45	48	52
648798	644986	641624	640343	639234	649420	640263	640953	643374	646531

Table 6. 10-Total cost of the process in \$/year

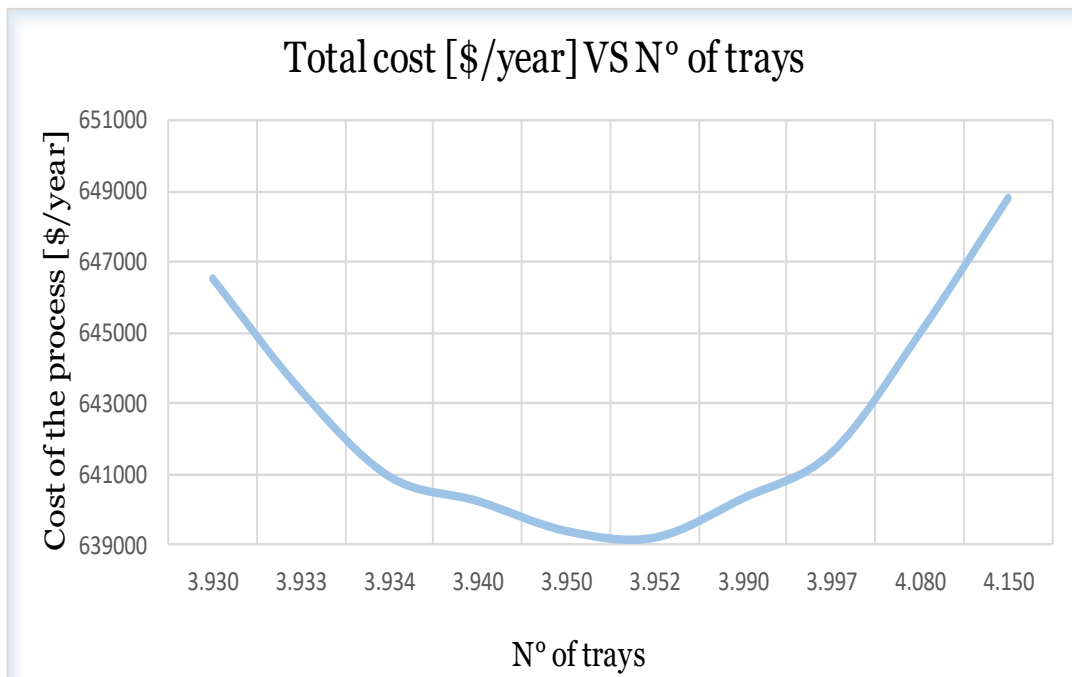


Figure 6. 8-Total cost in \$/year in the function of the number of trays

Configuration from 37 to 41 trays have a lower investment cost respect to the cheaper ones, but higher operative cost; differently configuration from 43 to 52 have lower operating cost but higher investment cost. In Figure 6.9 the trends of reflux ratio in the function of the number of trays are illustrated. As said before, the reflux ratio decreases with increasing the number of trays. The bigger column has many trays to obtain acetone on the top of the column and so need a fewer reflux ratio and so a fewer duty of condenser and reboiler.

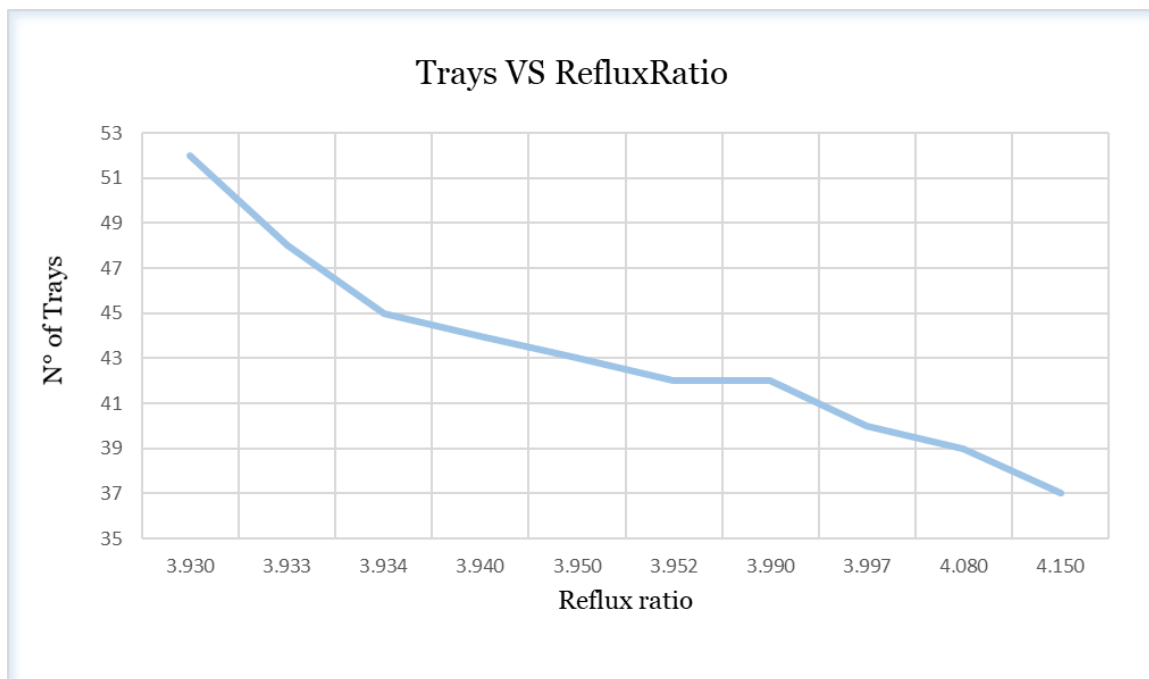


Figure 6. 9-Trays VS Reflux Ratio

6.2 Annual CO₂ emission of Divided Wall Column in nominal condition

Global Warming mitigation has increased the will to use renewable energy worldwide. Transportation is responsible for an estimated 14% of the global GHG (Green House Gas) emission, and biofuel has seen as an option to decrease these types of emissions. European Union, for example, has the aim to reduce to 10% the emission due to transportation until 2020. Biobutanol, produced by the ABE mixture is one of the best biofuels for this aim. The air-fuel ratio of butanol is higher than that of ethanol, which is the most common biofuel used, that the ON (octane number) is lower than the ethanol one. To reduce the environmental impact, that in this process is due to the GHG emissions, the entire LCA (life cycle assessment) of biobutanol was studied by Vaisanen et al. [57]. The only difference with this thesis is the use of DWC, whose emission will be analyzed in this paragraph. To evaluate the environmental impact of a DWC there isn't a unique way [58]. Firstly, because the steam used for the reboiler can be generated from different sources such as coal, Heavy Fuel Oil or Natural Gas, and then because the compressor used as a heat pump can be either steam turbine driving or electricity driving [59]. Furthermore, the utilized electricity can be generated by either traditional energy resources or a new one such as wind sea or biological sources. In this work the used methods are:

- Natural Gas, the most common source, is used to supply energy to reboiler, though Heavy Fuel Oil has a bigger net having value and would give a greater value of CO₂ emissions.
- For the condenser, an electrical compressor is used to bring water in the component.

The approximate amount of CO₂ emission has been calculated following equation 6.10, used from Gadalla et al. [60], in this equation the value of CO₂ emission is in kg_{CO₂}/h:

$$CO_2 emission = \left(\frac{Q_{fuel}}{NHV} \right) \left(\frac{C\%}{100} \right) \alpha \quad (6.10)$$

Which α represents the molar masses of CO₂-to-C ratio (cf. Equation 6.11):

$$\alpha = \frac{PMCO_2}{PMC} = 3.67 \quad (6.11)$$

NHV is the net heating value, and it is equal to 51600 kJ/kg for Natural Gas (NG) and 39771 kJ/kg for Heavy Fuel Oil (HFO) [60]. C% is the carbon content and depend as the previous parameter on the type of fuel, it is equal to 75.4 for NG and 86.5 for HFO. Q_{fuel} [kJ/h] is the heat duty of fuel consumed in the process has been calculated as follow (cf. Equation 6.12):

$$Q_{fuel} = \left(\frac{Q_{reb}}{\lambda_{steam}} \right) (h_{steam} - 419) \left(\frac{T_F - T_0}{T_F - T_S} \right) \quad (6.12)$$

λ_{steam} is the latent heat of the steam in kJ/kg, h_{steam} is the enthalpy of the steam and 419 is the enthalpy of water at 327.15 K both in kJ/kg. Q_{reb} always in kJ/h is the duty of the reboiler, that as is said before decreases with the increasing of the trays. At least, T_F is the flame temperature, T_S is the stack temperature and T_0 is the standard temperature. In Table 6.11 the values of these parameters are illustrated. Then in Table 6.12 the value of emissions for reboiler for all configuration (the same studied for the economic assessment) is shown.

Index for CO₂ emission calculation of reboiler

α	3.67
λ [kJ/kg]	2132.95 [61]
T_F [K]	2073.15 [58]
T_o [K]	298.15 [58]
T_s [K]	433.15 [58]

Table 6. 11-Index for CO₂ emission calculation for reboiler

CO₂ emission for reboiler

Trays	37	39	40	41	42	43	44	45	48	52
Q_{Reb} [Kj/h]	7.9E06	7.8E06	7.78E06	7.75E06	7.73E06	7.72E06	7.72E06	7.72E06	7.71E06	7.71E06
Q_{fuel} [Kj/h]	9298379	9200501	9102623	9068366	9048791	9037045	9034109	9029215	9024321	9019427
Emission [kg/h]	498	493	488	486	485	484	484	484	483	483

Table 6. 12-CO₂ emission for the reboiler

The emission depending proportionally on the reboiler duty (cf. Figure 6.10 (A)), increases with the decrease of the number of trays (as the operative cost). But as Figure 6.10(B) illustrates the bigger decrease is before column with 42 trays than as before, the decreasing is minimal, from 485 kg/h to 483 kg/h.

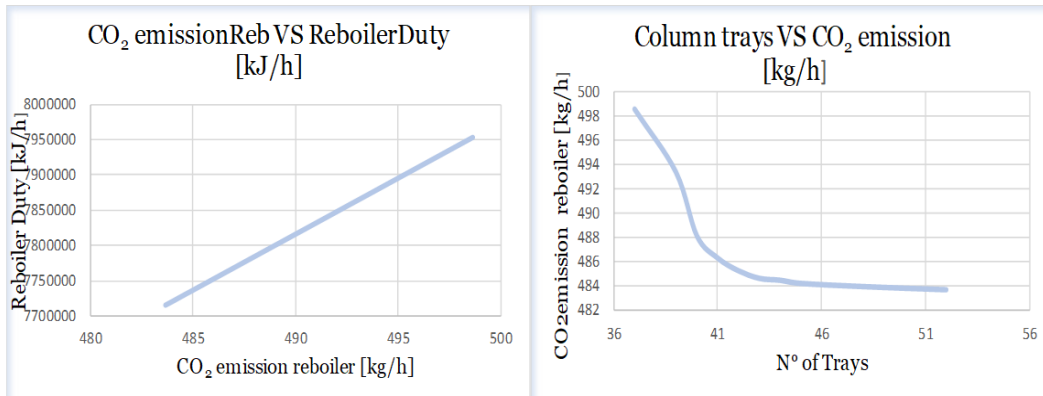


Figure 6. 10-(A) CO₂ emission of Reboiler in the function of the duty of the reboiler, (B) Column Trays in function of CO₂ emission

As far as concern the condenser, the emissions refer to the electric power which bring water to the component. Once the Data has been found the power in GJ/h will be multiplied for 51.1 kgCO₂/GJ [62].

CO₂ Emissions for Condenser

Trays	37	38	40	41	42	43	44	45	48	52
Qcon[J/s]	1.86E6	1.83E6	1.81E6	1.8E6	1.79E6	1.79E6	1.79E6	1.79E6	1.79E6	1.79E6
dt [k]	31.201	31.2	31.199	31.198	31.198	31.198	31.198	31.197	31.197	31.197
m [kg/s]	14.24	14.06	13.88	13.80	13.76	13.72	13.72	13.72	13.71	13.71
Q[W]	139.73	137.99	136.25	135.38	135.0	134.68	134.68	134.59	134.59	134.54
Q [J/h]	503060	496788	490515	487387	486223	484871	484871	484541	484541	484352
Emission [kg/h]	25.706	25.385	25.065	24.905	24.846	24.776	24.776	24.760	24.760	24.750

Table 6. 13-CO₂ emission for the condenser in kg/h

In Table 6.13 the emission of CO₂ due to the compressor used to bring water in the condenser is illustrated. This value, like the previous, decreases with

the number of trays. Also, in this case, after the column with 42 trays, the decrease is minimal. Figure 6.11 shown the two trends for the condenser, CO₂ emission in the function of duty of condenser and in function of N° of trays, the variation has the same trend of the reboiler one. By comparing these two terms of emissions, it can be seen then that relating to the condenser will have much lower weight respect to that of the reboiler for the total calculation of the emissions. In Table 6.14 a Figure 6.12 the value and trend for the total CO₂ emissions are shown.

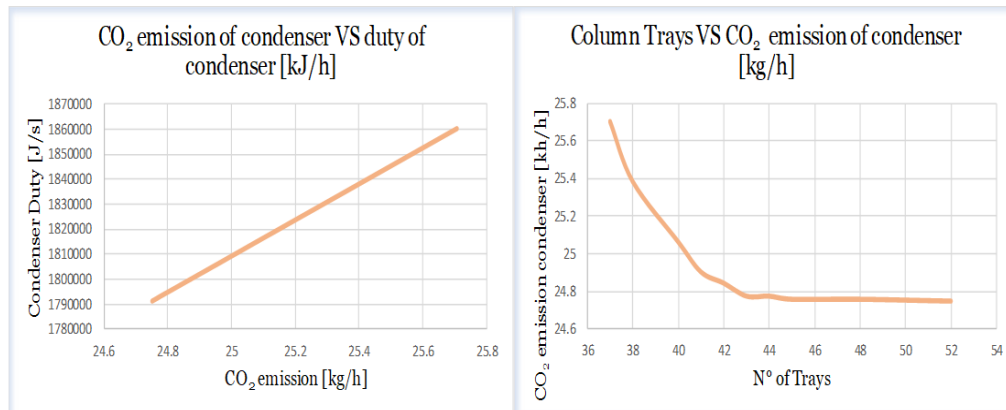
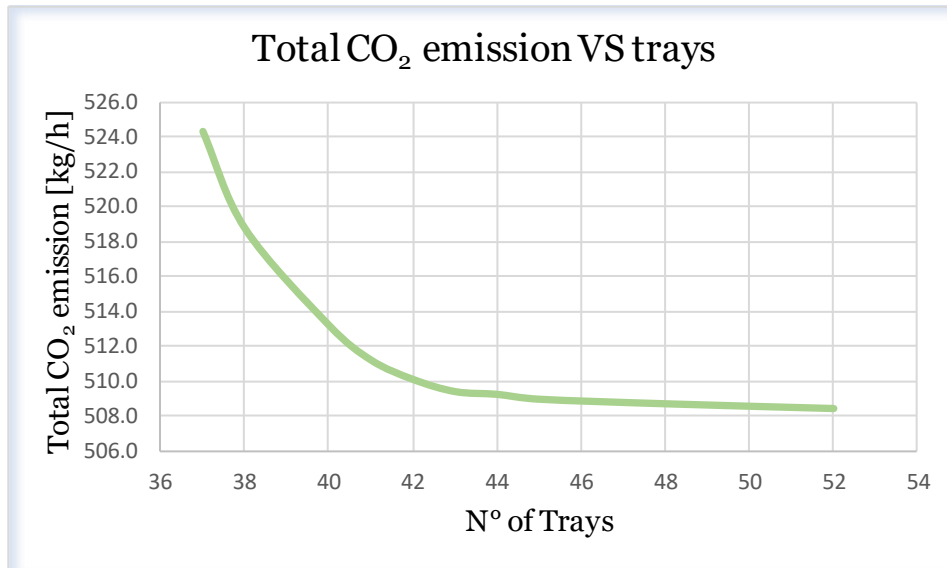


Figure 6. 11-Trends for compressor used to bring water to the condenser in kg/h, (A) CO₂ emission in function of duty of condenser, (B) CO₂ emission in function of number of trays

Total CO₂ emissions [kg/h]										
Trays	37	38	40	41	42	43	44	45	48	52
TOT_{emission}	524.4	518.8	513.2	511.2	510.1	509.4	509.3	509.0	508.7	508.4

Table 6. 14-Total CO₂ emission [kg/h]

Figure 6. 12-Total CO₂ emission in kg/h

As the total emissions demonstrate, biobutanol production brings to a decreasing in GHG emission respect to Diesel and Gasoline, which are usually used for transportation. [63]. Biobutanol, differently from ethanol can be used together with petrol and can be used with that in the vehicle. So, the potential for biobutanol use is very considerable. As far as concern the optimization, in this case, the column with 52 trays has low emissions, but after column with 42 trays, the decreasing is very low.

6.3 Comparison between DWC and indirect configuration for butanol production from ABE mixture

The most common design for biobutanol production from ABE is the train of the column. It can be used directly or indirectly. Di pretoro et al. [49] analyzed the indirect configuration to obtain biobutanol. In this design, there is a sequential recovery from the heaviest (butanol) in the first column, to the lightest (acetone) in the second one. To do a comparison with DWC, the train of the column was simulated in SimCentral, this process has the same operative condition illustrated in Table 5.7 and 5.8 for the DWC. Regarding the specification it is also the same as the previous study:

- Mass fraction of acetone in distillate = 0.995, mass fraction of butanol in bottom = 0.99
- Recovery ratio of acetone = 0.985, recovery ratio of butanol = 0.964

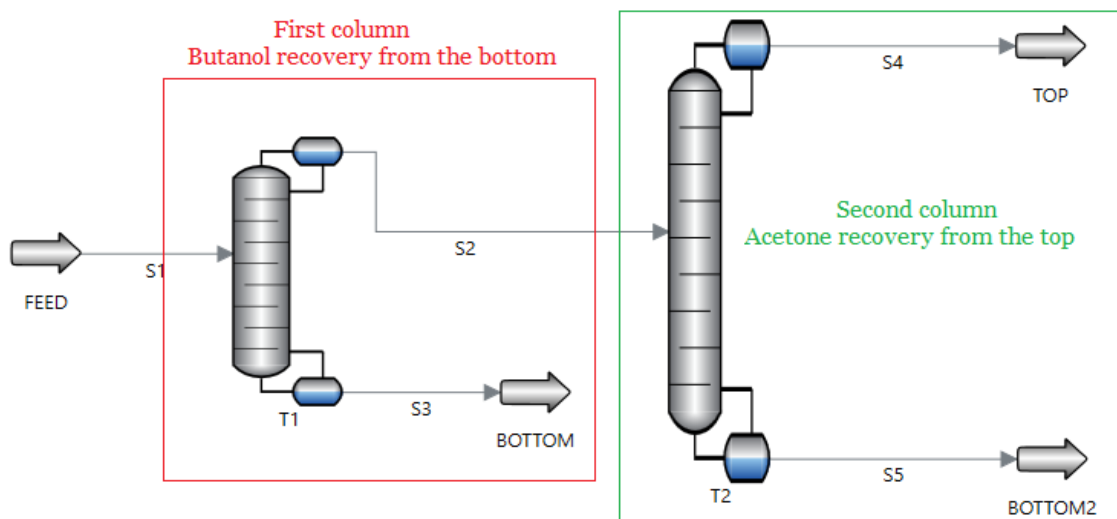


Figure 6. 13-Layout of indirect configuration in SimCentral software simulation

In Figure 6.13 the SimCentral layout of indirect configuration is exposed, the red zone is the first column for butanol recovery from the bottom, then the green zone, ha the aim of acetone recovery from the top. As it is possible to see in Figure 6.14 this configuration in optimal condition has bigger price respect to the DWC configuration. As said in literature the economic saving of DWC, is of 30% [12] respect to the indirect configuration, and this is supported by the obtaining number:

- 910894 \$/year for indirect configuration
- 639234 \$/year for DWC.

Both CAPEX and OPEX are affected by the design of two columns instead of one.

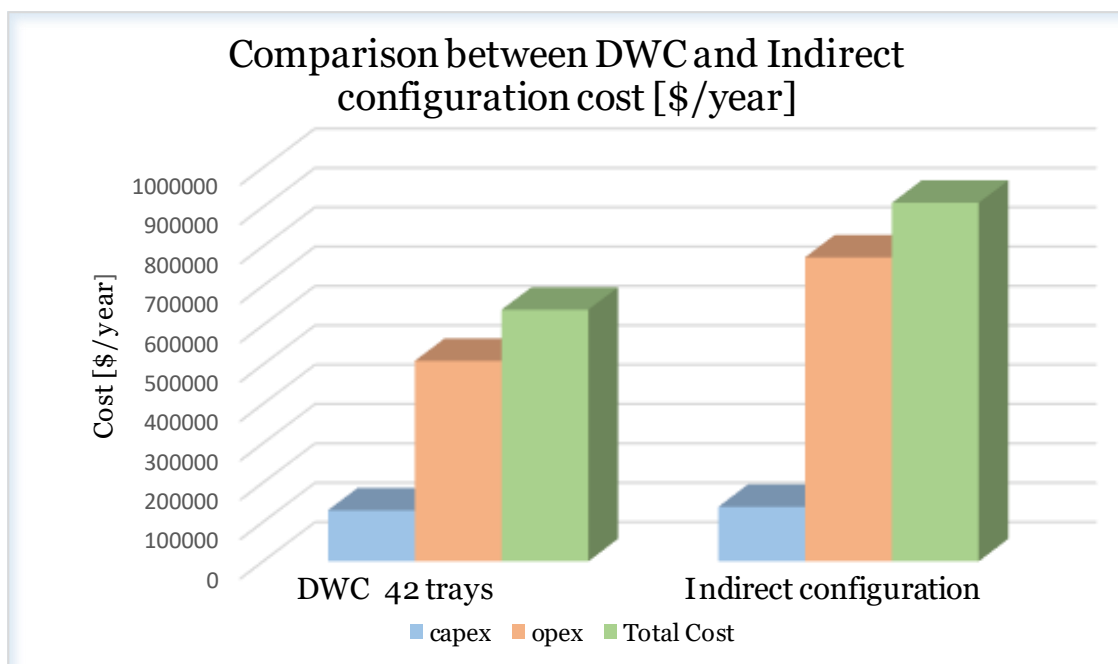


Figure 6. 14-Comparison between DWC and Indirect configuration cost [\$/year]

In Figure 6.15 with the same method, the comparison between emissions of CO₂ for the different designs is illustrated. Also, in this case, the DWC column shows a lower emission expressed in kg/h. The term which refers to the compressor is almost the same for the two configurations, but the reboiler

emissions of indirect configuration are almost twice of the DWC configuration ones.

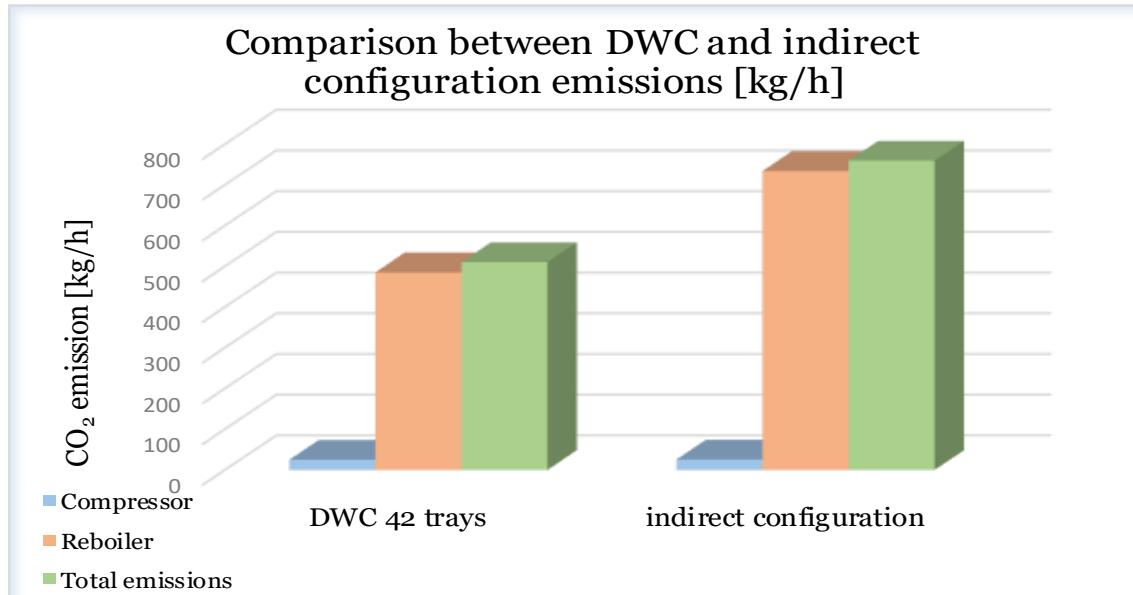


Figure 6. 15-Comparison between DWC and indirect configuration emissions [kg/h]

CHAPTER 7

**FLEXIBILITY ASSESSMENT AND
OPTIMIZATION**

In order to have a uniform overview for process optimization, it is useful to study the behavior of a configuration when determining variables are modified. The analyses that will be conducted in this chapter are focused on the flexibility of the proposed case study and the evolution of investment costs to be incurred in case of perturbations. Once these operations are carried out, there will be an integration of the environmental aspect with the study of the variations of CO₂ equivalent emissions related to the changes in the variables selected. The second part will deal with the comparison with the distillation of the ABE/W mixture with indirect configuration and the search for the best economical and flexible between different columns with a different number of trays. The research, as it is understood, is aimed at the economy, flexibility, and environmental impact. The indexes applied for the flexibility study are the Resilience Index and the Swaney & Grossman index, in Chapter 1 is proposed a theoretical explanation. For the evaluation of the costs, CAPEX and OPEX will be appointed and its numerical evaluation is not reported for redundancy (see Chapter 6).

7.1 Divided wall column case study

In Chapter 6, the best configuration optimized in nominal conditions for the separation of ABE/W mixture in a divided wall column is the tower with 42 trays. To understand the distillation related application of the flexibility indexes, the 42-trays DWC has been analyzed in detail. The nominal feed stream is defined by compositions and conditions in Table 5.7 and 5.8. The recovery and purity specifications are the following:

- Mass fraction of acetone in distillate = 0.995
- Mass fraction of butanol in bottom = 0.99
- Recovery ratio of acetone = 0.985
- The recovery ratio of butanol = 0.9604

These product requirements are to be maintained even in conditions of perturbations, otherwise, it would decay the principle of flexibility for a plant. The most critical parameters chosen for the analysis are water and butanol feed content. These flowrate variations are the most related to the upstream process and as mentioned in Chapter 4, the thermodynamics of the ABE/W mixture is critical when varying these two components for the presence of azeotropes. For the flexibility study is necessary to create a perturbations matrix; resulting from two perturbations vectors, referred to the water and butanol flowrate deviation. These vectors are built with the values of the perturbed variable from a \pm percentual deviation starting from the nominal condition, i.e. in the case of water is been made starting from 44.724 kmol/h and by varying this data with a \pm 10% of deviations with a step of 0.5 kmol/h. Below, Table 7.3 describes the expected variation ranges $\Delta\theta^{+/-k}$.

Parameter θ	Value θ^N	Expected deviation $\Delta\theta^{+/-k}$	Step	Unit
Butane flowrate	220.781	$\pm 14.2675\% \pm 31.5$	3.5	Kmol/h
Water flowrate	44.742	$\pm 10.0577\% \pm 4.5$	0.5	Kmol/h

Table 7. 1- Uncertain parameter θ^k

With this choice of flow-step for each component, the vector created is 19 x 1. The matrix associated has 19 columns and rows, this creates 361 (19 x 19) perturbation cases to analyze. At the center of the matrix, the nominal one is present. The SimCentral simulation of the 42-trays DWC result to be feasible, converges with a physical solution, in 334 of 361 perturbation cases (cf. Figure 7.1).

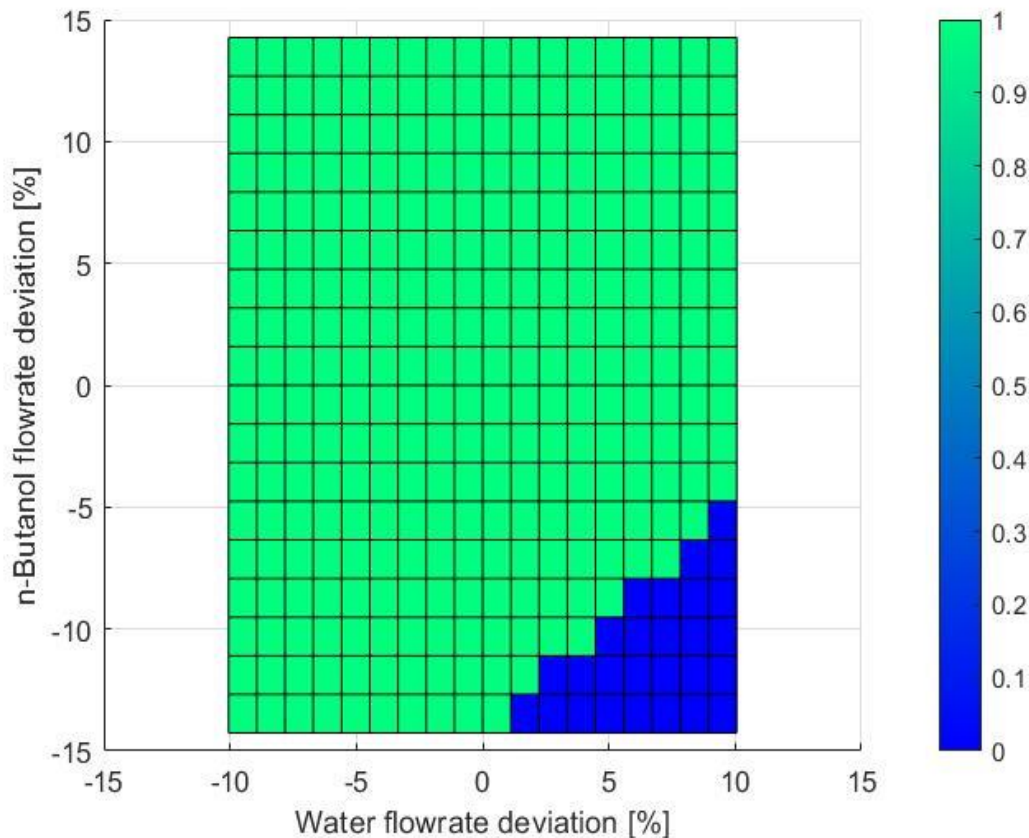


Figure 7. 1-Matrix of Feasibility

With a proper deviation range discretization, several simulations were performed, the green squares represent the feasible and operable case while the blue corresponds to operating conditions that didn't allow the specifications achievement. Notably, the unfeasible zones have a low ratio between flowrate of butanol and water. In Figure 7.2 is represented the same matrix of Figure 7.1 but with a different point of view: the ratio B/W instead of process feasibility. In general, this ratio in the matrix varies from the range of 3.84 and 6.27; the yellow zone is near 6 while the darker the blue the value is near 4. In the zone corresponding to unfeasibility in Figure 7.1 the ratio is between 3.84 and 4.2. When butanol lowers its concentration in feed and the water content rises the process became thermodynamically unfeasible for the presence of azeotropes.

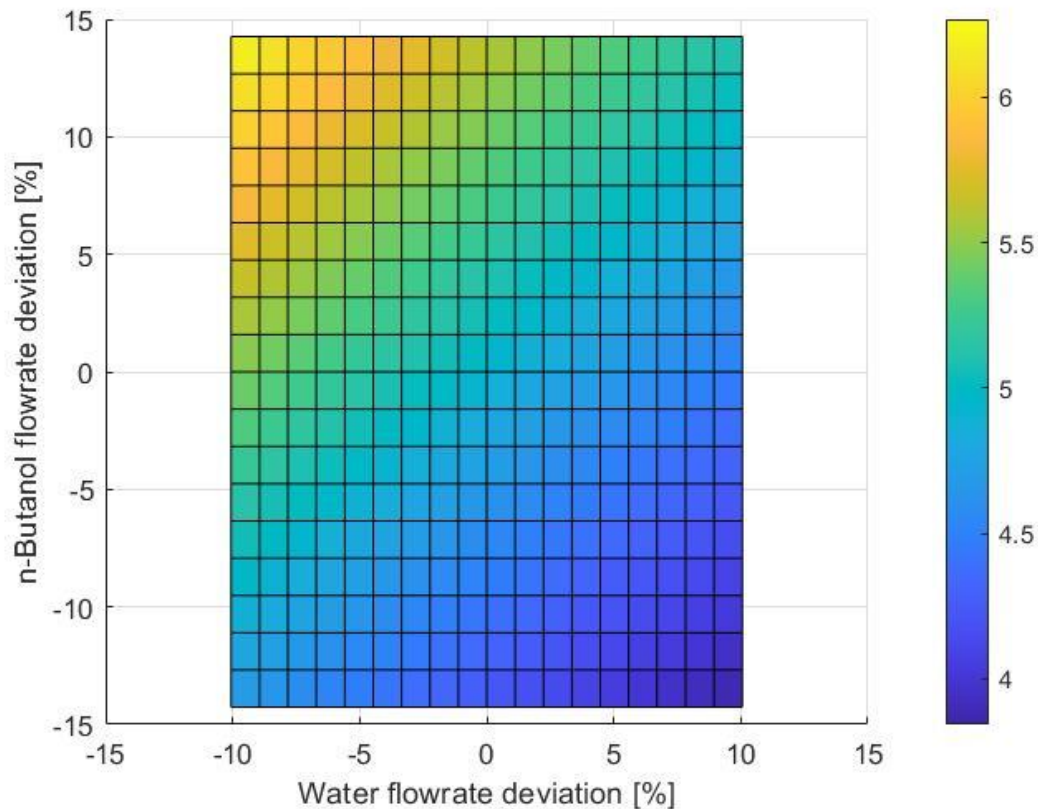


Figure 7. 2- Butanol-Water Ratio relative to deviations

The feasibility of the plant requires an increase of CAPEX and OPEX since changing the inlet specifications, maintaining the same purity requirements, involves higher heat transfer to reboiler and condenser. In terms of capital cost, the investment is in the resizing (area, number of tubes) of equipment while the term affecting operating costs is the increased demand for steam in the reboiler and cold water in the condenser. To have a more feasible process, the total cost investments to support will increase proportionally to the disturbance conditions furthest from the nominal ones, more feasibility means more economics loads. In Figures 7.4 and 7.5 the total and relative cost deviation, normalized concerning the nominal conditions, are represented as a function of the disturbance magnitude. To simplify graphics for readers, the highest cost items have been cut out. This operation has been made in the critical part of the perturbation matrix, where the total and the relative costs

have a value in the order of $5 \cdot 10^6$ \$/y and $5 \cdot 10^3$ % of deviation cost respectively.

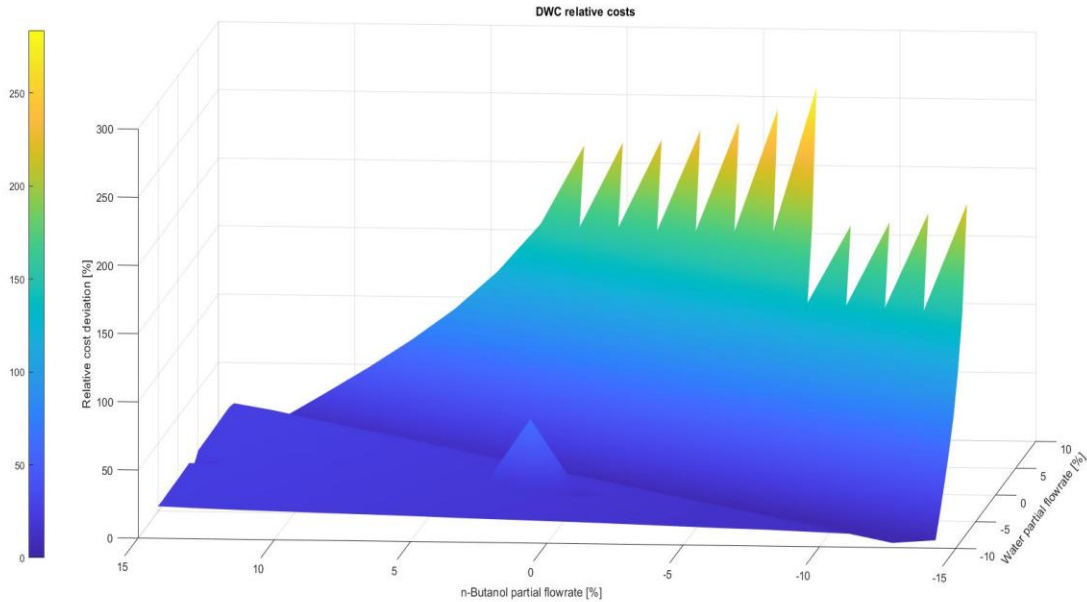


Figure 7. 3-Additional Costs

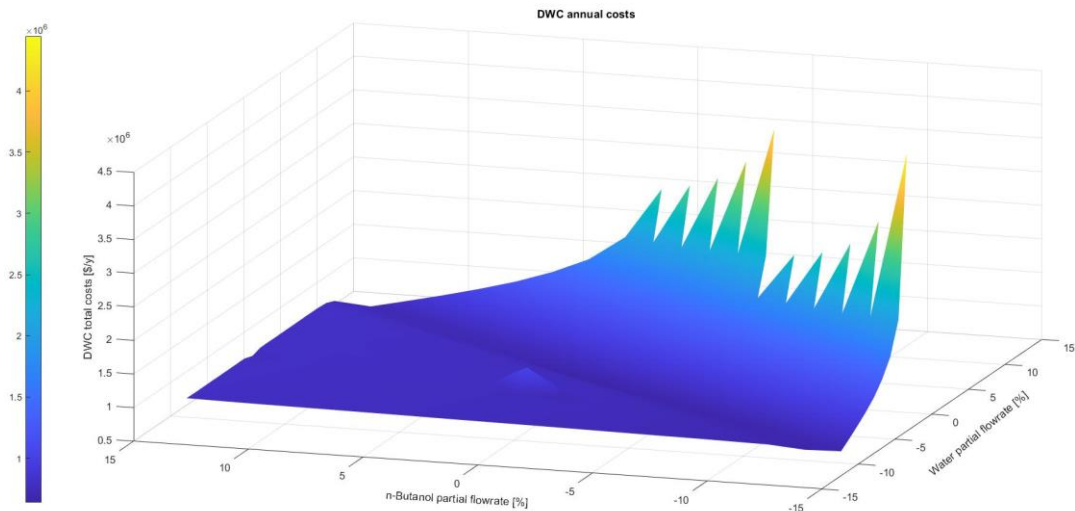


Figure 7. 4-Total Costs

It is notable by both graphs that the higher investment to do is in the areas where feed flowrates of butanol decrease and water one increase. The highest values correspond to the border-line feasibility zones. The relative deviation

for reboiler and condenser transfer follows the trend of the relative cost deviation. Before having a flexibility assessment, it is important to observe how the condenser and reboiler exchange areas also vary with one-way perturbations to understand which of the two components has the most effect on costs. The mono-directional variation refers to the perturbation of only one component with the other one remaining at nominal conditions (see Figure 7.6).

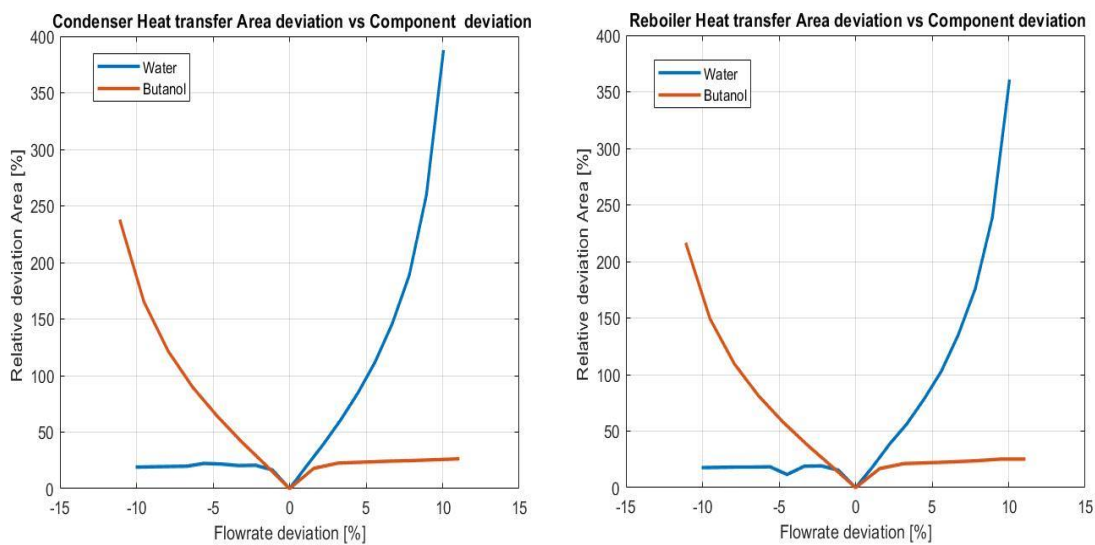


Figure 7. 5- Condenser and reboiler deviation area relative to one-way perturbations

The two graphs have the same trends, negative butanol deviation increase the heat transfer areas because less is its content in the feed more duties are necessary to obtain the high specification purity. An increase in water flowrate, with constant butanol, has the same effect on equipment. It's notable how water deviation flowrate has the greatest load for the design of the heat exchangers, its variation is more critical than considering also that the perturbation step for this compound is much lower than butanol. The same explanation can be conducted analyzing another key-factor: the column reflux. This parameter highlights the difficulty for a distillation tower to obtain purity, the higher it is, the more energy-intensive the process will be.

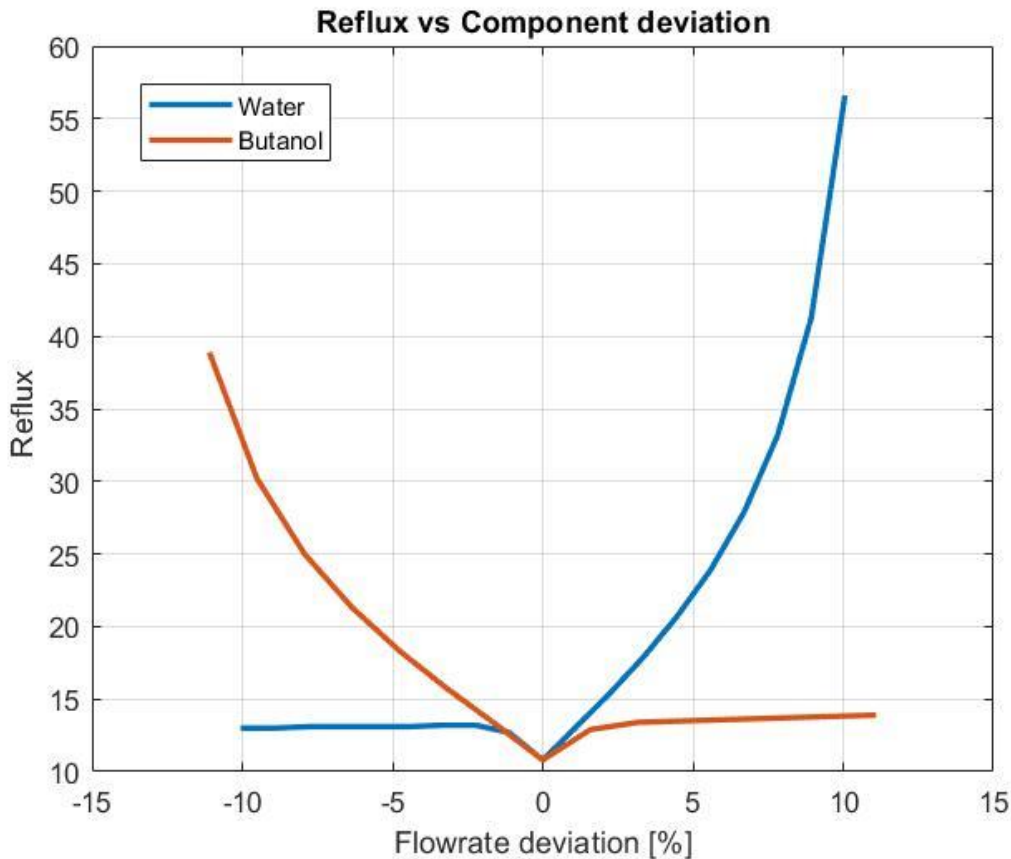


Figure 7. 6- Reflux deviation with one-way perturbations

The reflux ratio is already high under nominal conditions due to the high standard of purity required for the production of biobutanol; its value is increased up to 50 when the water concentration in the feed content increases with a deviation of the +10% or the butanol flowrate became -10% of the standard operating conditions. In chapter 6 an analysis of the process at an environmental level has been made, it is also interesting to note how carbon dioxide emissions vary with the perturbations. The CO₂ emitted depends on the energy requirements of the reboiler mainly, the condenser and the pump to transport cooling water. Therefore, it is expected a profile of polluting emissions that increase with larger deviations caused by higher energy load to be used. In the case of investments addressed to the flexibility of the

process in addition to the capital invested for equipment and duties, the increase in ecotaxes for environmental pollution must be considered.

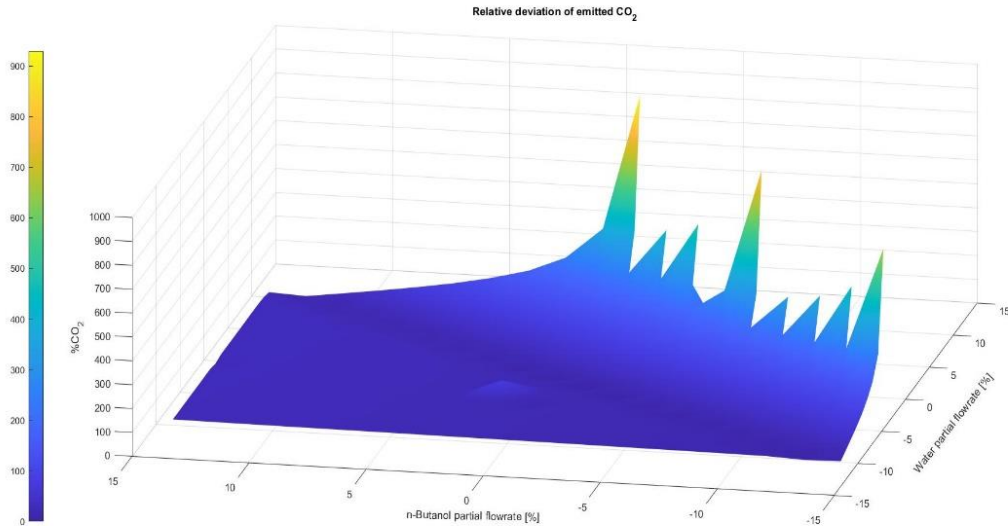


Figure 7. 7- Additional emissions related to flowrates deviations

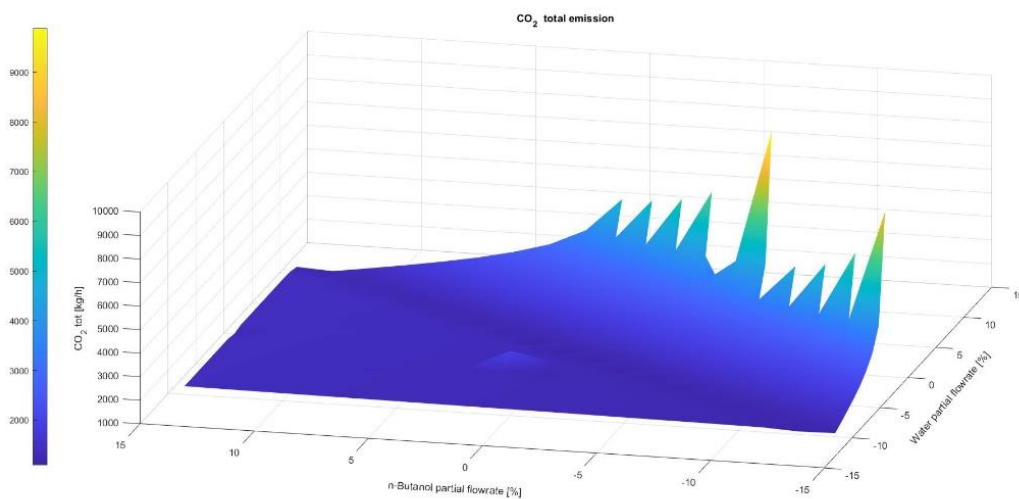


Figure 7. 8- Total emissions

Once understood the trends of the various factors mentioned above as the disturbance changes, it is possible to perform a flexibility analysis for the 42-trays divided wall column.

Flexibility analysis is coupled with the economic assessment according to the procedure suggested by Di Pretoro et al. [27]. The costs corresponding to

every perturbed operating condition were calculated and correlated to the different flexibility values by mean of the corresponding indexes. The plot represented in Fig 7.9 has the deterministic index, F_{sg} , and RI , in the function of the relative cost deviation. It is easier to observe the economic investment to effort and the relative percentual deviation and this is not misleading if the analysis is conducted for a single configuration.

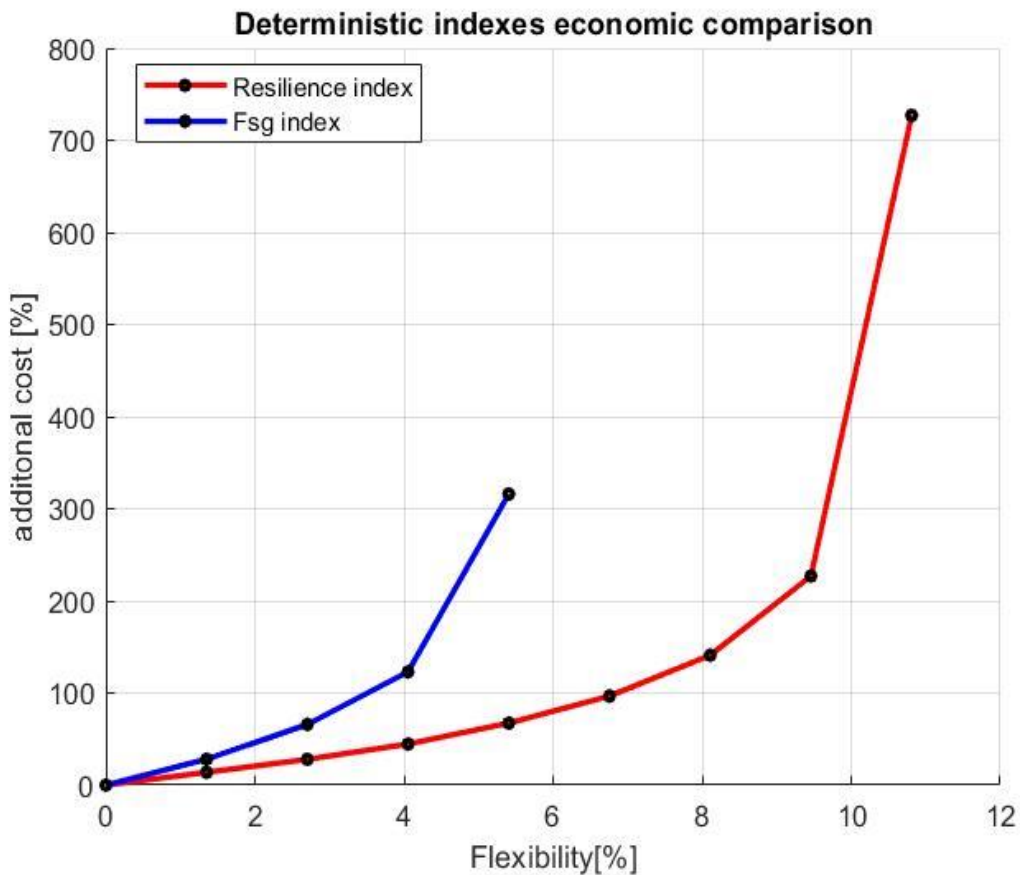


Figure 7. 9- Deterministic index comparison to additional costs

In data collection, other values for resilience index and F_{sg} exist but they represent the flexibility limit than can be overcome despite the non-affordability of a higher expense (order of $5 \cdot 10^3$ % than the nominal costs). The resulting Resilience Index for this case study is given by the largest total disturbance load not dependent by direction, see Chapter 1, and have a value

of 10.81. The maximum fraction expected that can be accommodated by the system in all the directions, F_{sg} index, is given by:

$$F_{sg} = \frac{\text{allowed deviation}}{\text{expected deviation}} = \frac{5.41}{12.16} = 0.44 \quad (7.1)$$

The blue line represents the flexibility index while the red one is relative to the Resilience index. As expected by their definition the F_{sg} index results more conservative than the RI one. Moreover, in both cases, it can be noticed that after 4% flexibility (9% for RI) much higher additional investments are required for a corresponding flexibility increase of one percentage point only. Even with low flexibility values, the relative costs immediately take on important values, e.g. from 0 % to 4 % for the F_{sg} , an investment of 200 % has to be made. Probably also the last values of each curve should be discarded because no economic-industrial plans would invest such a high percentage of investments to support 1% more flexibility. Another important thing to clarify is that the perturbation matrix was created with high flowrate variations for the respective components, this partly justifies the high investment costs required, paying 100% more for 1% flexibility means ensuring high feed variations (± 3.5 kmol/h for the butanol and ± 0.5 kmol/h for water) concerning the complexity of the thermodynamics of ABE/W.

7.2 Flexibility comparison with Indirect Configuration

In this paragraph, an economic comparison will be made between the 42-trays DWC and the indirect configuration (cf. Figure 6.13) in non-operating conditions. The nominal physical-chemical conditions and perturbed variables of the indirect configuration are the same as those of the divided wall column (see Table 5.7 and 5.8). To analyze flexibility, the same method explained in section 7.1 was used, the cost and feasibility data related to variable changes were taken from the work done by Di Pretoro et al. [49]. The first thing to observe is the feasibility domain, represented in Fig.7.10 which is different from that of the divided wall column.

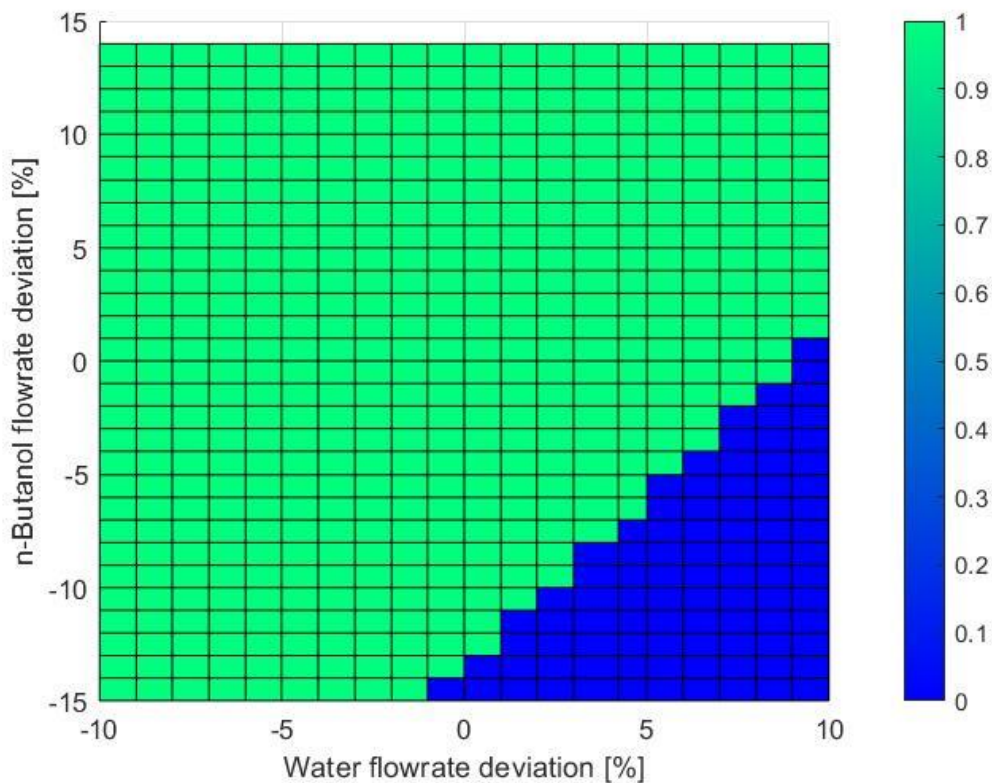


Figure 7. 10-Indirect configuration feasibility

This configuration results slightly less flexible, there are more blue zones (infeasibility zones) than the divided wall column, see Figure 7.1. This reduced operability area may be due to the remixing effect, which is present in series

column configurations. However, this difference is not so large and allows the economic comparison. The parameters studied are the deterministic parameters of Resilience and Swaney and Grossman. In this case, although comparing different systems, the graphs have been realized with the flexibility indexes coupled to the total costs normalized with that of the divided wall column configuration. In this way, it is possible to observe the percentages of variation of investment starting from a common base, which is the object of study of this work.

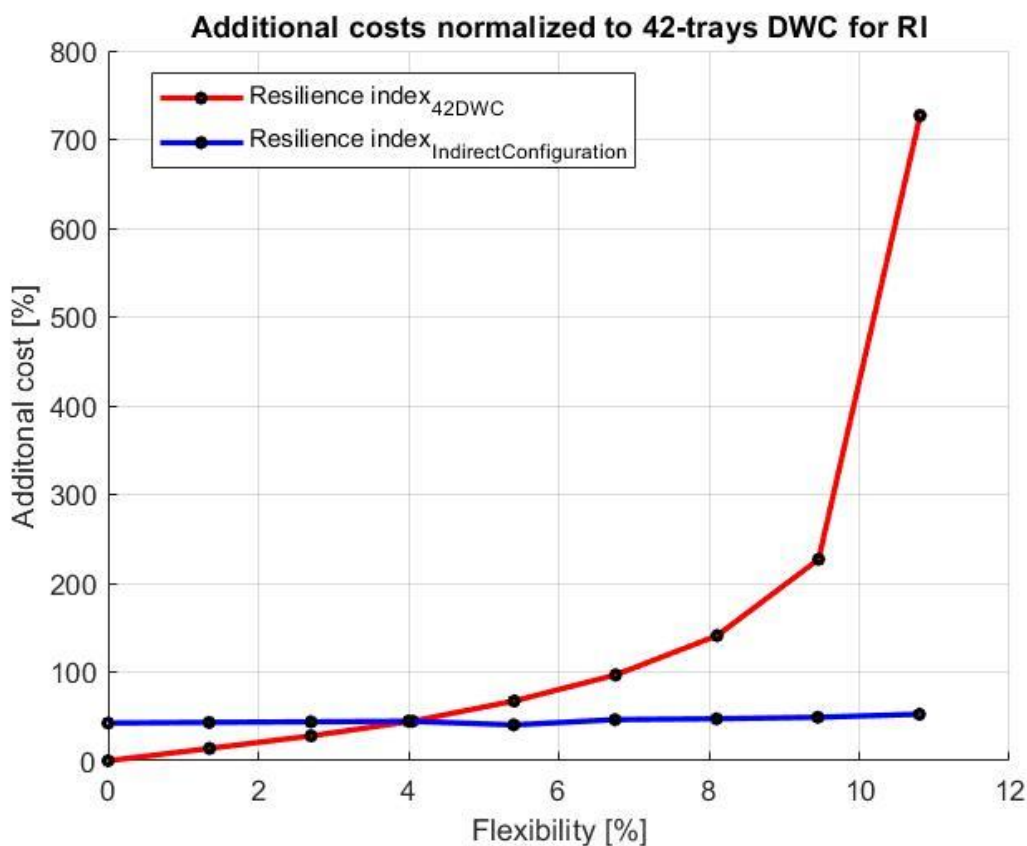


Figure 7. 11-Resilience Index with additional costs normalized

Regarding the resilience index, the total costs of the DWC are lower up to a $RI=4$, when the two curves intersect. When this value is reached, the trend changes as the indirect configuration costs much less. The behaviour of the 2 profiles is different: the indirect configuration requires a smaller investment gap (around 10%), compared to its starting condition, to cover the whole

range of flexibility set; while DWC configuration to get more flexibility requires investments in much higher percentage points, to go from 0 to 7 % of flexibility double its total costs. The differences in additional cost trends are mainly due to the fact the divided wall column is an integrated process: the indirect configuration has two condensers and two reboilers on which it is possible to better manage the external users while in the wall column this is limited. Having fewer degrees of freedom to manage has as a consequence a higher percentage increase in investment costs. The key-reading to the graph is that up to certain values of flexibility the direct configuration requires less total costs but a similar-exponential distribution of investments; on the contrary, the set of columns needs higher capital costs but maintains a linear additional costs trend, as flexibility changes until the value of 4% of flexibility. After this value is more optimized the second configuration.

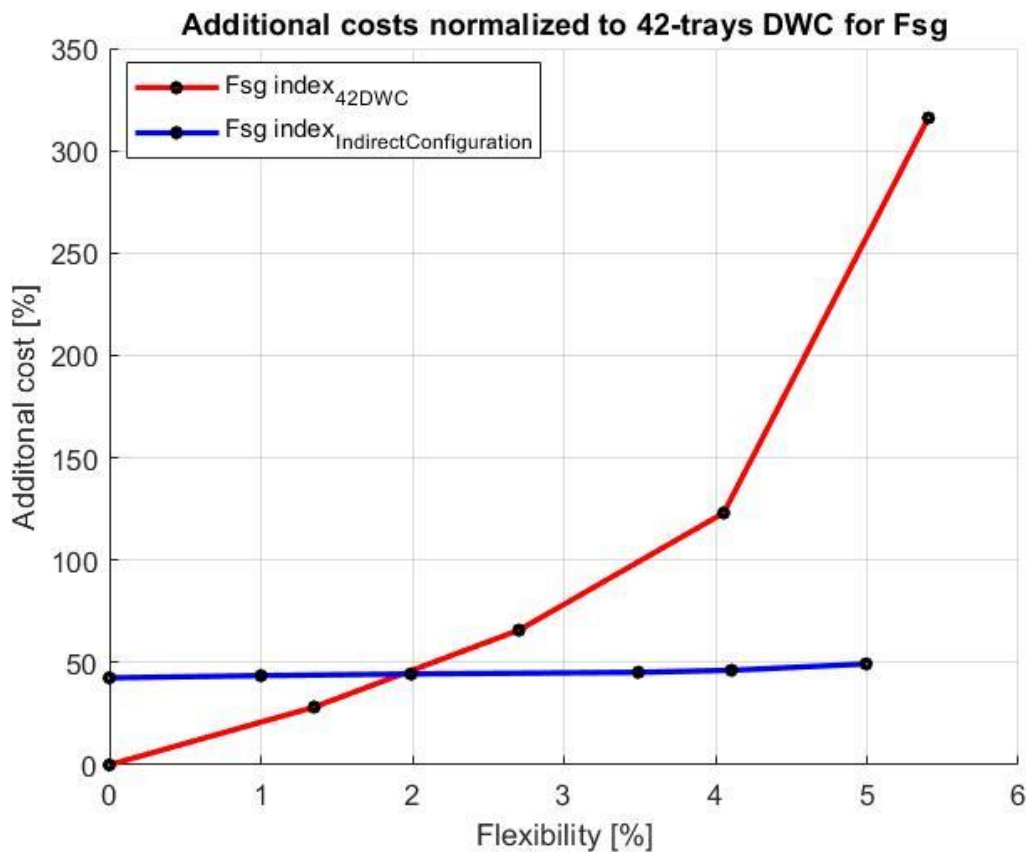


Figure 7. 12- F_{sg} Index with additional costs normalized

In the analysis with Swaney and Grossman index, the same trends as described above can be highlighted. Notably, the indirect configuration in the nominal condition has an additional cost of 45% than the divided wall column. The DWC column is slightly more flexible, but with high additional costs (in the order of 300%), which is why the hypothesis of supporting such a high economic effort would decay.

7.3 Study of the optimum flexibility configuration

This paragraph will analyze the best configuration, among three choices, that have advantages in terms of flexibility, costs and environmental emissions. In addition to assessing the configuration of paragraph 7.1, the other two choices were 37 and 52 trays. The selections are dictated by the optimal range, from 37 to 52, of divided wall column simulations able to reach the desired specifications. The three configurations are identical in terms of physical and chemical nominal conditions, what changes is just the number of trays. Being an economic comparison between three different columns, the graphs made for the flexibility indices are based on additional costs normalized with the 42-trays configuration, since each column has a different nominal cost due to the different properties.

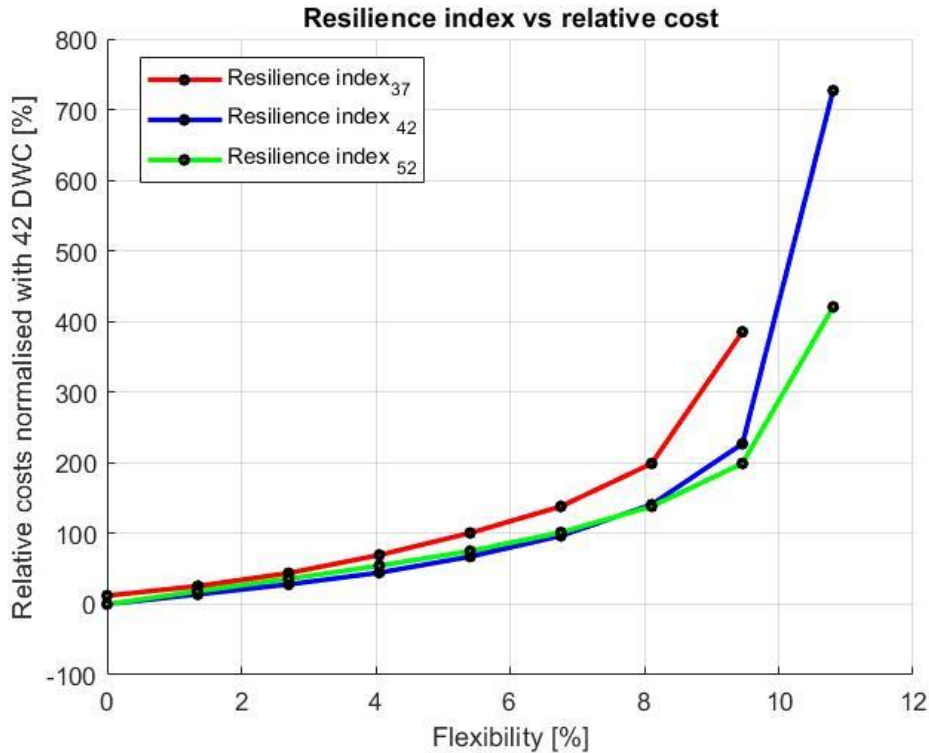


Figure 7. 13- Resilience index for the three configurations

Figure 7.13 is plotted the trends of RI with relative costs for the three configurations: the red line is for 37 trays, blue for 42 and green for 52. Notably, the configuration with fewer trays has less flexibility than others and its total costs are always greater for every percentage of flexibility that increases. The blue and green curves have about the same costs up to a resilience index of 9.5, then the configuration with 42 trays increases its costs much more evidently than 52 to get to the higher flexibility index (700% vs 400% normalized to the nominal condition). The economic evaluation concludes with the fact that configuration 52-trays is the one that supports the perturbations with a lower investment, therefore the most optimal for the resilience index analysis. The same analysis is led to the F_{sg} index in Figure 7.14.

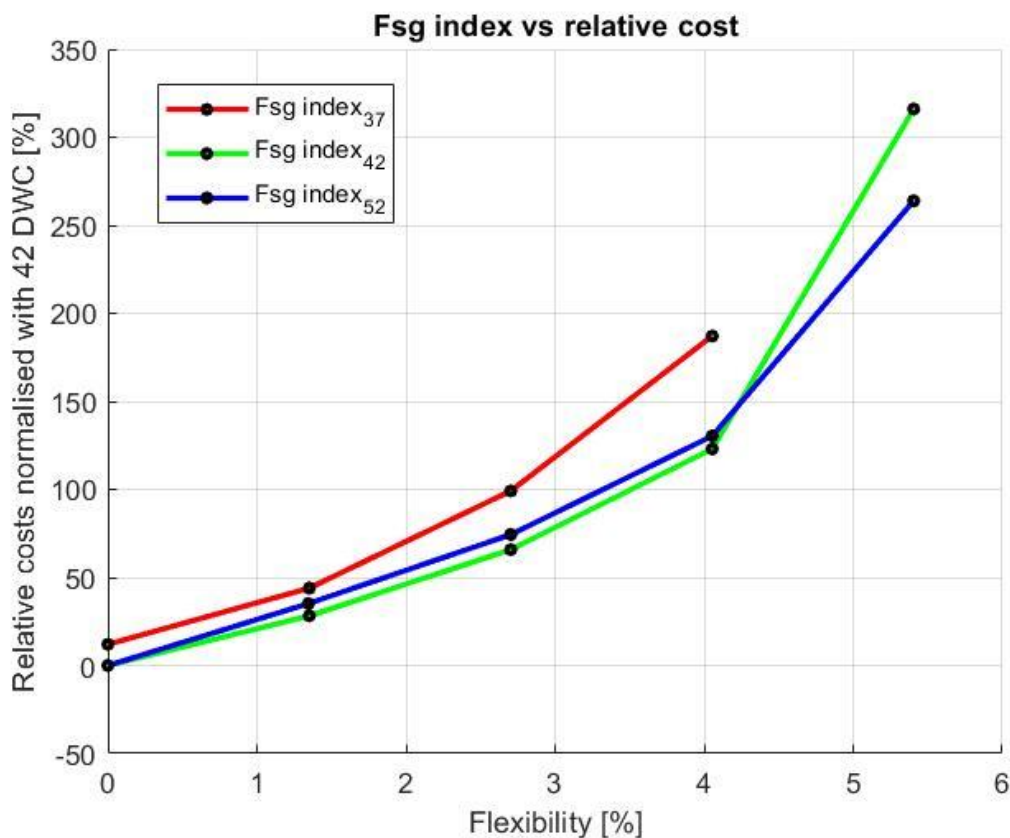
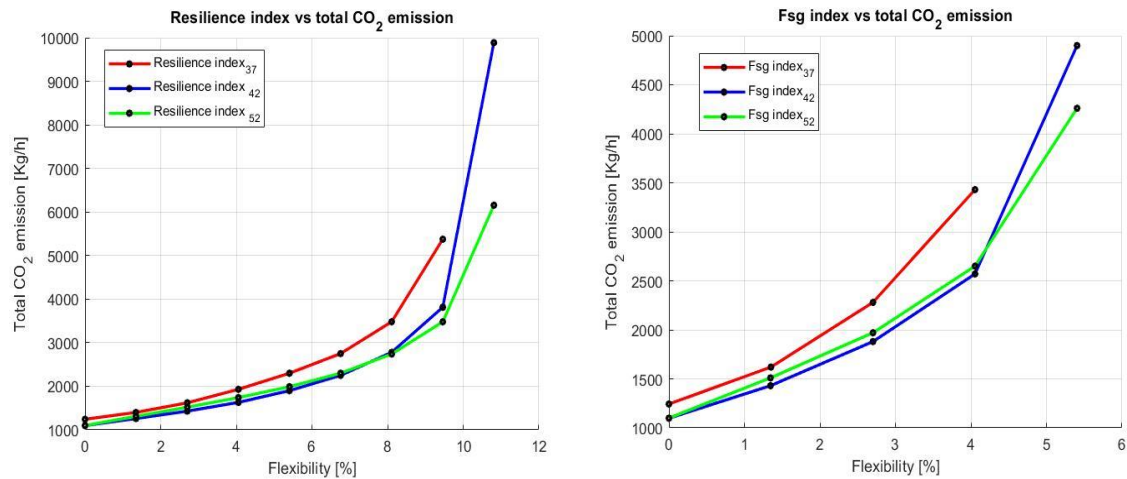


Figure 7. 14- Resilience index for the three configurations

The trends are very similar also with the F_{sg} analysis: 37-trays column is the highest in additional costs and reaches lower flexibility than the others. It's important to point out that the curves with the Swaney and Grossman index show higher cost values for the type of flexibility analysis done: RI takes the maximum disturbance value regardless of the direction it has while F_{sg} considers flexibility on all directions of the disturbance, for example, a value of 3 means that the process is feasible for all variations of 3% that may be. The profiles of the green and blue curves are similar but the 52-trays with the same flexibility costs slightly more. This similarity stops after index 4.05 because as before there is a higher increase by the 42-trays, however, the economic gap with the other one is reduced unlike the graph with the RI index. Although the gap is smaller, it can be stated that the 52-trays configuration, even if it costs more at parity indexes up to 4.05, is the most optimized. The research aims to have more flexibility, in this case, if the purpose is to stop at an F_{sg} of 4.05 the choice would fall on configuration 42. To have a robust analysis of optimal flexibility it is necessary to consider also how emissions vary with the indexes; a column may be more economically advantageous, but it must also respect criteria on environmental impact, which are reflected in the ecotaxes to be paid. The total costs of DWC are very much linked to the not negligible impact of condenser, reboiler, and duties, which are the most important factors to take into account when calculating CO_2 emissions, so the emissions profiles should be similar to those of total costs. The graphic reported above in Figure 7.15 represents the total carbon dioxide plant emissions per hour as a function of RI and F_{sg} . As theoretically expected, the CO_2 emission profiles follow the total cost trend for both indices used. The only interesting difference to note is that the red curve is always above the other two, the solution with 37 plates does not guarantee at any point an environmental saving condition; on the contrary in the cost curves, in perturbation conditions close to the nominal ones, the three configurations intersected each other.

Figure 7. 15- Deterministic index with total CO₂ emissions

In conclusion, after a complete analysis, the column with 52-trays, among the three configurations evaluated, better meets the analysis criteria chosen between flexibility optimum, economic and environmental. These studies are focused on three principles, this does not mean that at the absolute level the column with more trays is always the best choice. Each chemical company has different needs, knows the ranges of deviation of the variables that could be perturbed, of the investments that it can support and therefore sets the best principle to find its optimum.

CHAPTER 8

CONCLUSIONS

In the previous chapters, all the aims for which this thesis has been programmed have been addressed. Most of the observable work was focused on the optimization under nominal and perturbed conditions of the divided wall column configuration. This treatment has given robust results confirming many of the theories seen in the bibliography. The least observable part of the work was the simulation of this configuration on computer programs; since there was no shortcut for the divided wall column the use of equivalent configurations was complex and very iterative to achieve stable convergence. Without the thermodynamic feasibility analysis, some subsequent studies would not have been addressed with the same rigor, it is important to study the starting point to better understand the problems afterward. All the discussion is about stationary conditions, the process and dynamic control section weren't the purposes of the work. From a nominal point of view, the analysis of the optimal configuration for the divided wall column, changing the number of trays, found in the 42-trays column the best design. This one saves 30 % of the total costs compared to the most commonly used indirect configuration for the ABE/W separation and, it is also beneficial for the reduction of pollutant emissions. About the perturbation conditions, for butanol and water inlet flowrate, it can be deduced that the divided wall column has a discrete range of feasibility and flexibility thanks to the study of Resilience Index and F_{sg} . Optimum flexibility analysis highlights that accurate oversizing can both save money in perturbed conditions and keep the environmental impacts of the chemical process relatively low. Indeed, the configuration with the lowest number of trays is the column with the highest economic and environmental impact load. The biggest problem in the flexibility of divided wall columns being the investment to be addressed as an integrated process. Future work could focus on optimization, in terms of additional costs, and the search for equally flexible design with a flatter cost trend. Ideas could be taken from integrated compression heat recovery cycles.

List of Indexes

CHAPTER 1

- θ^n nominal values of uncertain parameters
- $\Delta\theta^+, \Delta\theta^-$ expected deviation of each parameter
- d designed variable associated with equipment costs
- z controlled variables
- I set of equality constraints for plant and design
- J set of inequality constraints for plant and design
- T uncertain parameters range

CHAPTER 2

- L, V liquid and vapor flowrates
- j generic stage column
- H_j enthalpy of the stage j
- S_j side streams
- Q_{mj+1}^W heat transfer across the wall
- G_{jm} interlinking liquid and vapor flowrates
- N_T Total number of trays
- N_{Si} Number of trays of section i
- R_i Reflux ratio of vapor/liquid
- V_i Vapor flowrate of section i

L_i	Liquid flowrate of section i
S_i^L	Liquid-side stream of section i
S_i^V	Vapor-side stream of section i
l	Component flowrates in the liquid phase, kmol/h
v	Component flowrates in the vapor phase, kmol/h
H	Enthalpy of vapor, MJ/kmol
h	Enthalpy of liquid, MJ/kmol
P_i	Pressure above section i
V_{min}	Minimum vapor flowrate
N_{min}	Minimum number of trays
CHAPTER 4	
γ_i	activity coefficient
τ_{ij}	dimensionless interaction parameters
τ_{ji}	dimensionless interaction parameters
G_{ij}	Gibbs free energy
α_{ij}	non-randomness parameters
R	universal constant of the gas
T	absolute temperature
Δg_{ij}	interaction energy parameters
K_{ij}	Physical equilibrium constant

CHAPTER 6

C_{BM}	Bare module cost
C_{P^0}	Purchased cost
F_{BM}	The bare module cost factor
F_P	Pressure factor
F_M	Material factor
α	Molar masses CO ₂ -to-C
Q_{fuel}	Heat duty of the fuel
Q_{reb}	Heat duty of the reboiler
Q_{cond}	Heat duty of the condenser

Bibliography

- [1] Ye Ni, Zhihao Sun, *Recent progress on industrial fermentative production of acetone-butanol-ethanol by clostridium acetobutylicum*, 2009, pp 405-413
- [2] Kraemer, Harwardt, Bronneberg, Marquardt, *Separation of butanol from acetone-butanol-ethanol fermentation by a hybrid extraction-distillation process*, 2010, pp 949-963
- [3] Ezeji, Qureshi, Blaschek, *Butanol fermentation research: Upstream and Downstream manipulations*, 2004, pp 305-314
- [4] Xue, Zhao, Chen, Bai, Yang, Sun, *integrated butanol recovery for an advanced biofuel: current state and prospects*, 2014, pp 3463-3474
- [5] Qureshi, Blashek, *Butanol recovery from model solution/fermentation broth by evaporation: evaluation of membrane performance*, 2001, pp 175-184
- [6] Woods, *The genetic engineering of microbial solvent production*, 1995, pp 259-264
- [7] Groot W. J., van der Lans R. G. J. M., Luyben K. Ch. A. M., *Batch and continuous butanol fermentation with free cells: integration with product recovery by gas-stripping; Applied Microbiology and Biotechnology*, 1989, 32, 305-308.
- [8] Qureshi, Blaschek, *Production of acetone butanol ethanol (ABE) by a Hyper-production mutant strain of Clostridium beijerinckii BA101 and recovery by pervaporation*, 1999, pp 594-602
- [9] Daza Montano, *Process design and evaluation of butanol production from lignocellulosic biomass*, 2009
- [10] Errico, Sanchez-Ramirez, Quirez-Ramirez, Rong, Segovia-Hernandez, *Biobutanol purification by hybrid extraction-divided wall column configurations*, 2017, pp 1027-1032

- [11] Oak Ridge National Laboratory, *Materials for separation technologies: energy and emission reduction opportunities*, 2015
- [12] J. Zhou, H.A. Kooijman, R. Taylor, *Parallel column model for Dividing Wall Column simulations*, 2019
- [13] John G. Pendergast, David Vickery, *Consider dividing wall columns*, 2008
- [14] Alexandre Dimian, Costin Bilder, Anton Kiss, *Integrated Design and Simulation of Chemical Processes*, 2014
- [15] ÖmerYildirim, Anton A.Kiss, Eugeny Y.Kenig, *Dividing wall columns in the chemical process industry: A review on current activities*,2011
- [16] Roomi Kalita, Joseph C. Gentry, *Dividing Wall Columns in Operation*, 2018
- [17] Shin, J.; Lee, J.; Lee, S.; Lee, B.; Lee, M, *Enhance operation and reliability of dividing-wall columns*, 2013, 85–88
- [18] Dwivedi, Strandberg, Halvorsen, Preisig, Skogestad, S. *Active Vapor Split Control for Dividing-Wall Columns*, 2012
- [19] Huaqiang, Xiangwu, Nan, Wenyi, *Experimental study on vapor splitter in packed divided wall column*, 2016, J. Chem. Technol. Biotechnol, 91, 449–455.
- [20] Ki Joon Kang, Gregorius Rionugroho, Harvianto Moonyong Lee, *Hydraulic Driven Active Vapor Distributor for Enhancing Operability of a Dividing Wall Column*,2017
- [21] Veniamin D. Dimitriadis, Efstratios N. Pistikopoulos, *Flexibility analysis of dynamic systems*, 1995
- [22] Swaney, R.E., Grossmann, I.E., *An index for operational flexibility in chemical process design. part i: formulation and theory*, 1985a
- [23] Grossmann, I.E., Floudas, C.A., *Active constraint strategy for flexibility analysis in chemical processes*, 1987

- [24] Pistikopoulos, E.N., Mazzuchi, T.A., *A novel flexibility analysis approach for processes with stochastic parameters*, 1990, *Comput. Chem. Eng*
- [25] Dimitriadis, V.D., Pistikopoulos, E.N., *Flexibility analysis of dynamic systems*, 1995, *Ind. Eng. Chem. Res.*
- [26] Lai, S.M., Hui, C.-W., *Process flexibility for multivariable systems*, 2008, *Ind. Eng. Chem. Res.* 47 (12), 4170–4183
- [27] Alessandro Di Pretoro, Ludovic Montastruc, Flavio Manenti, Xavier Joulia, *Flexibility analysis of a distillation column: Indexes comparison and economic assessment*, 2019
- [28] Schultz, M.A., O'Brien, D.E., Hoehn, R.K., et al., *Innovative flow schemes using dividing wall columns*, 2006, *Computer Aided Chemical Engineering*, 695–700
- [29] Strandberg, J. and Skogestad, *Stabilizing operation of a 4-product integrated Kaibel column*, 2006
- [30] Jobson, M., *Dividing wall distillation coming of age*, 2005
- [31] Kaibel, B., Jansen, H., Zich, E., and Oulijić, Z., *Unfixed dividing wall technology for packed and tray distillation columns*, 2006
- [32] Mutalib, M.I.A. and Smith, R., *Operation, and Control of Divided Wall Distillation Columns. Part 1: Degree of Freedom and Dynamic Simulation*, 1998, *Trans. IChemE*, vol. 76, p. 308.
- [33] Howard, G. M., 1967, *Ind Eng Chem Fundam*, 6(1): 86.
- [34] Woff and Skogestad, *Operation of integrated three product distillation columns*, 1995, vol. 48p 6034
- [35] Sangal, Kumar, Mishra, *Divided wall distillation column: Rationalization of the degree of freedom analysis*, 2011, pp 319-328, 2011
- [36] Kiss, A. A., *Advance distillation technologies: Design control and applications*, 2013, John Wiley and Sons.
- [37] Petlyuk, F, *Distillation theory and its application to the optimal design of separation units*, 2004, Cambridge: Cambridge University Press.

- [38] Yildirim, O. K. *Dividing wall columns in the chemical process industry*. (2011)
- [39] Dejanovic, I. M. (2010). *Dividing wall column- A break-throug towards sustainable distilling*. (2010)
- [40] Becker, H. a. *Partitioned distillation columns- Why, when and how*. (2001) Journal of Chemical Engineering.
- [41] C. Triantafyllou, R. S. *The design and optimization of a fully thermally coupled distillation column*. (1992)
- [42] Muelikeishna, K. M. *Development of dividing wall distillation column design space for a specified separation*.(2002) Chemical engineering research and design.
- [43] Mueller, I. a. *Reactive distillation is a dividing wall column – rate-based modeling and simulation*.(2007) Industrial & Engineering Chemistry Research.
- [44] Amminudin, K. a. *Design and optimization of fully thermally coupled distillation columns.Part 2: Application of dividing wall columns in the retrofit*. (2001) Chemical Engineering Research and Design.
- [45] Sotudeh, N. a. (2008). *Extension of a method for the design of divided wall columns*. Chemical Engineering and Technology.
- [46] Rangaiah, O. a. *A simplified procedure for the quick design of dividing wall columns for industrial applications*.(2009) Chemical Product and Process Modeling.
- [47] Halvorsen, I. a. *Energy efficient distillation*.(2011) Journal of Natural Gas Science and Engineering.
- [48] Halvorsen, I. a. *Minimum energy consumption in multicomponent distillation. 1. Vmin diagram for a two-product column*.(2003) Industrial and Engineering Chemistry Research.
- [49] Di Pretoro A., Montastruc L., Manenti F.; Joulia X., *Flexibility Assessment of a Biorefinery Distillation Train: Optimal Design under Uncertain Conditions*, 2019.

- [50] Stichlmair and Fair, *Distillation: Principles and Practical*, 1998.
- [51] Errico, M., Sanchez-Ramirez, Quirez-Ramirez, Rong, Segovia-Hernandez, *Multiobjective Optimal Acetone-Butanol-Ethanol separation using Liquid-Liquid Extraction-Assisted Divided Wall Columns*, 2017.
- [52] Chinedu, O. Okoli, Thomas A. Adams II, *Design of dividing wall columns for butanol recovery in thermochemical biomass to butanol process*, 2015.
- [53] Sangal V.K., Kumarb V., Mani Mishrab I., *Optimization of structural and operational variables for the energy efficiency of a divided wall distillation column* (2011), Computers and Chemical Engineering
- [54] Bauer M.H., and Stichlmair J., *Design and economic optimization of azeotropic distillation processes using mixed-integer nonlinear programming* (1997), *Computers Chem. Engng* Vol. 22, No. 9, pp. 1271-1286
- [55] Dejanovic, I.; Matijasevic, L.; Halvorsen, I. J.; Skogestad, S.; Jansen, H.; Kaibel, B.; Olujic, Z. *Designing four-product dividing wall columns for the separation of a multicomponent aromatics mixture* (2011) *Chem Eng Res Des*, pp 89, 1155.
- [56] Turton R., Bailie R.C., Whiting W.C., Shaeiwitz J.A., Batthacharyya D., *“Analysis Synthesis, and design od chemical processes”*, (2012), fourth edition, Prentice hall.
- [57] Vaisanen s., J. Havukainen, V. Uusitalo, M. Havukainen, R. Soukka, M. Luoranen, *“Carbon footprint of biobutanol by ABE fermentation from corn and sugarcane”* (2015), Lappeenranta University of Technology, LUT Energy, Laboratory of Environmental Technology, P.O. Box 20 FI-53851, Lappeenranta, Finland.
- [58] Yang A., Shirui Sun, Ali Eslamimanesh, Shun'an Wei, Weifeng Shen. *“Energy-saving investigation for diethyl carbonate synthesis through the reactive dividing wall column combining the vapor recompression heat pump or different pressure thermally coupled technique”*, (2019).
- [59] Oluji_Z., Sun L, Rijke A., Jansens PJ. *“Conceptual design of an internally heat integrated propylene-propane splitter Energy”* (2006).

[60] Gadalla M, Olujić Z, Derijke A, Jansens P. *“Reducing CO₂ emissions of internally heat-integrated distillation columns for the separation of close boiling mixtures Energy”* (2006)

[61] https://www.thermexcel.com/english/tables/vap_eau.htm

[62] Waheed M.A., Oni A.O., Adejuyigbe S.B., Adewumi B.A., Fadare D.A., *“Performance enhancement of a vapor recompression heat pump”* (2014), Applied energy

[63] <http://www.isprambiente.gov.it/contentfiles/00003900/3906rapporti-03-28.pdf>