

POLITECNICO DI MILANO
School of Industrial and Information Engineering
Department of Chemistry, Materials and Chemical Engineering
“Giulio Natta”
Master of Science in Chemical Engineering



**Design, simulation and optimization
of an azeotropic distillation section
for biorefinery processes**

SuPER
Sustainable Process Engineering Research

Supervisor :
Prof. Flavio MANENTI
Co-supervisor :
Ing. Alessandro DI PRETORO

Candidate :
Vitor LACERDA MAURICIO
Matr. n. 903335

Academic Year 2019–2020

This thesis is dedicated

to my wife Lais and our child, that is growing inside her beautiful belly

“What I’m getting at is that people have to come up with a clever strategy if they want what they know and what they don’t know to live together in peace. And that strategy—yep, you’ve got it!— is thinking.”

(Haruki Murakami, *Sputnik Sweetheart*, p. 145, 2001)

Contents

Contents	I
List of Figures	IV
List of Tables	VII
Abstract	IX
Estratto	XI
1 Introduction	1
1.1 The energy transition challenge and the Biorefinery role . . .	1
1.2 Butanol as alternative (bio)fuel	6
1.2.1 Butanol Production and the ABE Process	7
1.2.2 Biobutanol production challenges	8
1.3 Scope of the work	12

2	Distillation of Azeotropes	14
2.1	Distillation and the Vapor-Liquid Equilibrium	14
2.1.1	Determination of liquid and vapor compositions of VLE	18
2.2	Azeotropic mixtures	20
2.3	Azeotropic distillation	23
3	Separation process of water and butanol	26
3.1	Azeotropic distillation of water–butanol mixture	26
3.2	Process description	28
3.3	Phase equilibrium of water–butanol mixture	29
3.4	Equipment control philosophy	31
4	Process Simulation	36
4.1	Simulation software	38
4.2	Strategies for convergence	41
4.3	Process Flow Diagrams	45
4.4	Steady-state results	50
4.4.1	The base case	50
4.4.2	Condenser and reboiler evaluation	54
4.4.3	Sensitivity analysis and design optimization	58
4.4.4	Comparison of results from both simulators	62

<i>CONTENTS</i>	III
5 Process Dynamics	66
5.1 Pressure-driven simulations	66
5.1.1 Fluid Flow Simulation	69
5.1.2 Dynamic Simulation	70
5.2 Equipment Sizing	71
5.3 Cost evaluation	72
6 Conclusions	77

List of Figures

1.1	Conversion of major components in cellulosic biomass to reactive intermediates (Ginley and Cahen, 2011)	3
1.2	Routes and products of thermochemical and hydrolysis processing of lignocellulose (Bharathiraja <i>et al.</i> , 2017)	5
1.3	Energy demand of various processes for separating butano from ABE fermentation broth	11
2.1	Standard distillation column, showing the internal flows of vapor and liquid. (Green and Perry, 2007)	15
2.2	x-y Diagram for generic components i and j for different relative volatility (α) values.	17
2.3	x-y Diagram for VLE of Ethyl Acetate-Ethanol mixture at 1 kgf/cm^2 (101.3 kPa) using Soave-Redlich-Kowng Equation of State.	21
2.4	T-x-y Diagram for minimum boiling azeotrope mixture of Ethyl Acetate-Ethanol at 1 kgf/cm^2 (101.3 kPa).	21
2.5	x-y Diagram for VLE of Chloroform-Acetone mixture at 1 kgf/cm^2 (101.3 kPa) using NRTL activity model and ideal gas law.	22

2.6	T-x-y Diagram for maximum boiling azeotrope mixture of Chloroform-Acetone at 1 kgf/cm^2 (101.3 kPa).	22
2.7	Schematic concept of a Dividing Wall Column. (Yildirim <i>et al.</i> , 2011)	25
3.1	Process flow diagram of proposed azeotropic distillation section for water-butanol mixture (di Pretoro, 2017)	27
3.2	T-x-y Diagram of water-butanol mixture as obtained from standard NRTL parameters of PRO/II simulator	31
3.3	Experimental and regression data of water-butanol VLLE, as obtained by Boffa, 2015	32
3.4	Proposed azeotropic distillation control strategy	35
4.1	Equilibrium-stage model of distillation columns (Green and Perry, 2007).	38
4.2	A stage of a non-equilibrium model of distillation columns (Green and Perry, 2007).	39
4.3	Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} < 0.1$ in PRO/II.	46
4.4	Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} > 0.1$ in PRO/II.	47
4.5	Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} < 0.1$ in SimCentral.	48
4.6	Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} > 0.1$ in SimCentral.	49

4.7	Temperature profile of water column and butanol column for base case	51
4.8	Composition profiles of liquid phase for the water column in the base case	52
4.9	Composition profiles of liquid phase for the butanol column in the base case	53
4.10	Flow profiles of liquid and vapor phases for the water column in the base case	53
4.11	Flow profiles of liquid and vapor phases for the butanol column in the base case	54
4.12	Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 2\%$ for different thermodynamic models	56
4.13	Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 10\%$ for different thermodynamic models	56
4.14	Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 40\%$ for different thermodynamic models	57
4.15	Flow rate to condenser versus condenser duty for different butanol fractions	58
4.16	Energy consumption for sensitivity analysis of the number of trays. Cases 1 to 7 are for $z_{BuOH} = 4\%$; cases 8 to 14 are for $z_{BuOH} = 40\%$	61
4.17	Temperature and flow rates profiles for the butanol column in the base case with $P = 1$ atm, as obtained in SimCentral . .	65
5.1	Detailed engineering PFD of water butanol separation process in SimCentral.	68

List of Tables

1.1	Selected physical properties of Butanol, Gasoline and Ethanol	6
3.1	Selected references on thermodynamic models for mixtures containing water and butanol	30
3.2	Parameters of NRTL model for water-butanol system with $\alpha = 0.2[kJ]$, as obtained by Boffa, 2015	31
4.1	Standard feed conditions for separation of water and butanol	50
4.2	Conditions and specifications for base case simulation	50
4.3	Steady-state results for main streams in the base case	51
4.4	Sensitivity analysis for the number of trays in each column	59
4.5	Sensitivity analysis for the pressure of both columns	62
4.6	Additional specifications for simulation in SimCentral - Process Mode	63
4.7	Compared results of base case with $P = 1$ atm for PRO/II and SimCentral	64
5.1	Distillation columns sizing	72

5.2	Heat Exchangers sizing	72
5.3	Three-phase separator (decanter) sizing	72
5.4	Parameters of Guthrie’s method for the selected equipment (M&S index of 2018 is considered in all cases)	74
5.5	Factors for d term of Guthrie’s method	74
5.6	Detailed CAPEX for the azeotropic distillation of water-butanol	75
5.7	Detailed OPEX for the azeotropic distillation of water-butanol	75
5.8	Estimated Total Annual Cost for the azeotropic distillation of water-butanol	75

Abstract

Renewable and sustainable fuels attract attention as oil substitutes due to their potential to impact positively the environmental challenges of our planet. In this context, the concept of Biorefinery was developed, in analogy to today's petroleum refineries, to produce chemicals and fuels starting from biomass as raw material. Among the potential products of interest, Butanol stands out particularly because of its characteristics, that classify it as a "drop-in" fuel, with significant advantages over bioethanol.

Biobutanol can be produced from the ABE fermentation process, after which it must be separated and purified. The present MSc. thesis investigates the design and optimization of an azeotropic distillation section to separate the mixture of water and butanol, that is generated from the separation plant of ABE. This additional process allows to increase the recovery of butanol, that is the most valuable of the fermentation products.

The work presents a brief investigation of the distillation operation, as well as the thermodynamics of vapor-liquid equilibrium and of azeotropes. Then, a process to separate water and butanol mixture, a heterogeneous maximum-boiling azeotrope, is devised, exploiting the phase separation and liquid-liquid equilibrium that is established.

The process is validated by means of steady-state simulation using two different commercial simulators. Results in terms of energy requirement are investigated, varying butanol concentration on the feed stream and the activity coefficient models for calculation. When compared to literature, the

proposed models provide coherent results, allowing the optimization by means of a sensitivity analysis of relevant variables. The results pointed out to the best design alternative that would generate the lowest energy requirement.

The optimized design is then detailed in terms of control scheme for the investigation using pressure-driven simulations. The results generated additional changes in the design to cope with the process dynamics. Finally, a preliminary cost estimation of installation and operation of the process is provided.

Estratto

Negli ultimi anni le fonti di energia rinnovabile stanno attirando molta attenzione come sostituti del petrolio grazie al loro impatto positivo in merito alle sfide ambientali del pianeta. In questo contesto, si è sviluppato il concetto di bioraffineria, in analogia alle raffinerie di petrolio, per produrre prodotti chimici e combustibili a partire dalla biomassa. Tra i potenziali prodotti, spicca particolarmente il biobutanolo grazie alle sue caratteristiche che lo classificano come combustibile “drop-in”, con notevoli vantaggi rispetto al bioetanolo.

Il biobutanolo può essere prodotto dal processo di fermentazione ABE, dopo il quale deve essere separato e purificato. La presente tesi indaga la progettazione e l’ottimizzazione di una sezione di distillazione azeotropica per separare la miscela di acqua e butanolo, generata dall’impianto di separazione di ABE. Questo processo aggiuntivo consente di aumentare il recupero del butanolo, che è il più prezioso dei prodotti di fermentazione.

Il lavoro presenta una breve indagine sull’operazione di distillazione, nonché sulla termodinamica dell’equilibrio liquido-vapore e degli azeotropi. È stato quindi ideato un processo per separare acqua e butanolo, miscela che presenta un azeotropo eterogeneo di massima, sfruttando la separazione di fase e l’equilibrio liquidoliquido si stabilisce.

Il processo viene convalidato mediante simulazione stazionaria utilizzando due diversi simulatori commerciali. Sono stati dunque studiati i risultati ottenuti in termini di fabbisogno energetico, variando la concentrazione di

butanolo nella alimentazione ed i modelli di coefficiente di attività. Rispetto alla letteratura, i modelli proposti consentono l'ottenimento di risultati coerenti con le prestazioni attese dal processo, permettendo così l'ottimizzazione mediante un'analisi di sensitività delle variabili più rilevanti. I risultati hanno indicato la migliore alternativa di progetto che fornisce il più basso consumo di energia.

Il progetto ottimizzato viene quindi dettagliato in termini di controllo per l'indagine utilizzando simulazioni basate sulle perdite di carico. I risultati hanno generato quindi ulteriori cambiamenti nel design per adeguarlo alle dinamiche di processo. Infine, viene fornita una stima approssimativa dei costi di installazione e funzionamento del processo.

Chapter 1

Introduction

1.1 The energy transition challenge and the Biorefinery role

Energy availability and consumption is directly related to a country's economic performance and the well-being of its citizens. As the demand for energy rises significantly —by a factor of 20 in the current millennium, while population has grown by a factor of 6, the interest in alternative sources of energy has also been growing. Among the various possibilities, renewable and sustainable fuels attract attention as oil substitutes due to their potential to impact positively the CO_2 -related environmental challenges of our planet, reducing the net carbon dioxide emissions, as well as assuring energy security (Ginley and Cahen, [2011](#)).

According to a report by the International Energy Agency, a growth in renewable power capacity of 50% is expected between 2019 and 2024, led by solar photovoltaic systems. The increase in the growth rate is strongly dependent on government policies, related to regulatory aspects, investment and system integration between different sources of energy. In 2018, renewable energy was responsible for 3,7% of transport fuel demand, of which 93% was provided by biofuels. In the same forecast period mentioned earlier, biofuels output should expand in 24%, to approximately 190 billion liters a year, although its share slightly decreases to 90% due to the expansion of electric

vehicles. Currently, United States and Brazil are the largest biofuel producers, while market prospects in China become continuously more relevant. Among the actions to accelerate fossil fuels substitution by biofuels are the greater use of the so-called “drop-in” fuels, i. e. fuels that can be used at higher blend percentages in traditional fossil fuels, or that can be used pure without modifications to engines or the existing fueling facilities (IEA, 2019).

Research and production of bioethanol and biodiesel are now consolidated, encouraged by past fluctuations of oil prices and governmental policies. They are currently the most technical and commercially feasible renewable fuels available, derived mainly from first generation crops —those also used for food production, such as soy beans, sugar cane or sugar beet (Taylor, 2008). Biofuels can also be obtained from second generation crops, that have no food use. They are based on the conversion based of lignocellulosic biomass through different technological routes, that eventually generate a number of co-products that can be recovered for economical uses. For this reason, researchers have envisioned the concept of production units analogous to today’s petroleum refineries: a central processing facility, with shared utilities, that could generate fuels and chemicals from biomass, conveniently called “Biorefinery”. Figure 1.1 illustrates a Biorefinery starting from biomass as raw material.

Unlikely its oil counterpart, Biorefineries do not need to be very large facilities. They can be dispersed and rely on local availability of biomass, which also contributes for increased energy security. To maximize flexibility, several bio-industries can be linked together, where the residue of one industry can serve as raw material for others (Cherubini, 2010). In fact, the International Energy Agency (IEA), defines Biorefinery as “the sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)”. In the light of this broad, holistic definition, a Biorefinery does not need to be a single industry, but can also be formed of several processes that are interconnected, starting from bio-based raw materials, generating valuable products and reducing

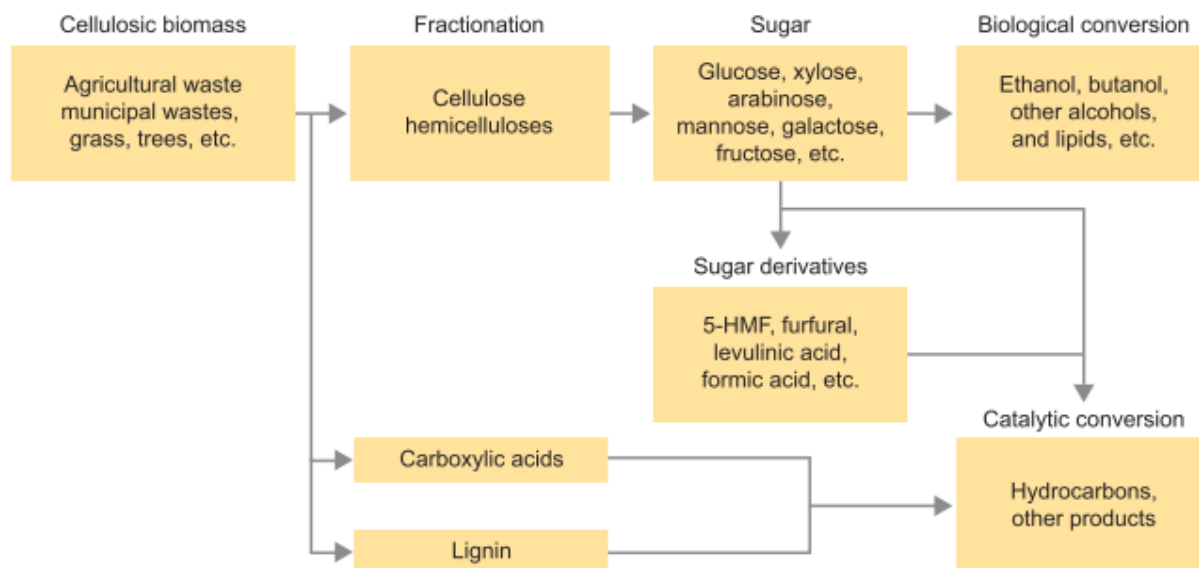


Figure 1.1: Conversion of major components in cellulosic biomass to reactive intermediates (Ginley and Cahen, 2011)

waste.

The conversion of biomass into different products can be done through several processes that can be divided into four major groups. First, thermochemical processes, of which gasification and pyrolysis are the main technologies. They consist in the use of high temperature (300–700°C) to produce liquid oil, light gases and syngas —a mixture of H_2 , CO , CO_2 and CH_4 —in their turn used directly as biofuel or as intermediate for other fuels (through Fischer-Tropsch process, for instance) and chemicals. This category also includes direct combustion for production of heat, the oldest and most common use of biomass.

Second, biochemical processes, that occur at lower temperatures, with lower reaction rates and, sometimes, low yields. Fermentation is the lead biochemical process, using microorganisms and/or enzymes to convert a fermentable broth into products, of which Ethanol is perhaps the most famous example.

Third, physical processes, that simply promote a size reduction or separa-

tion of feed stock biomass. Some lignocellulosic pre-treatment methods also fall under this category.

Fourth and last, chemical processes, that are those processes where substances are transformed into others by means of chemical reactions. The most common chemical processes are hydrolysis (with acids, alkalis or enzymes) and transesterification. The latter nowadays is a widespread technology for production of biodiesel from vegetable oils and waste fat (Cherubini, 2010). Examples of thermochemical and hydrolysis processes of lignocellulose for obtention of various products is illustrated in Figure 1.2.

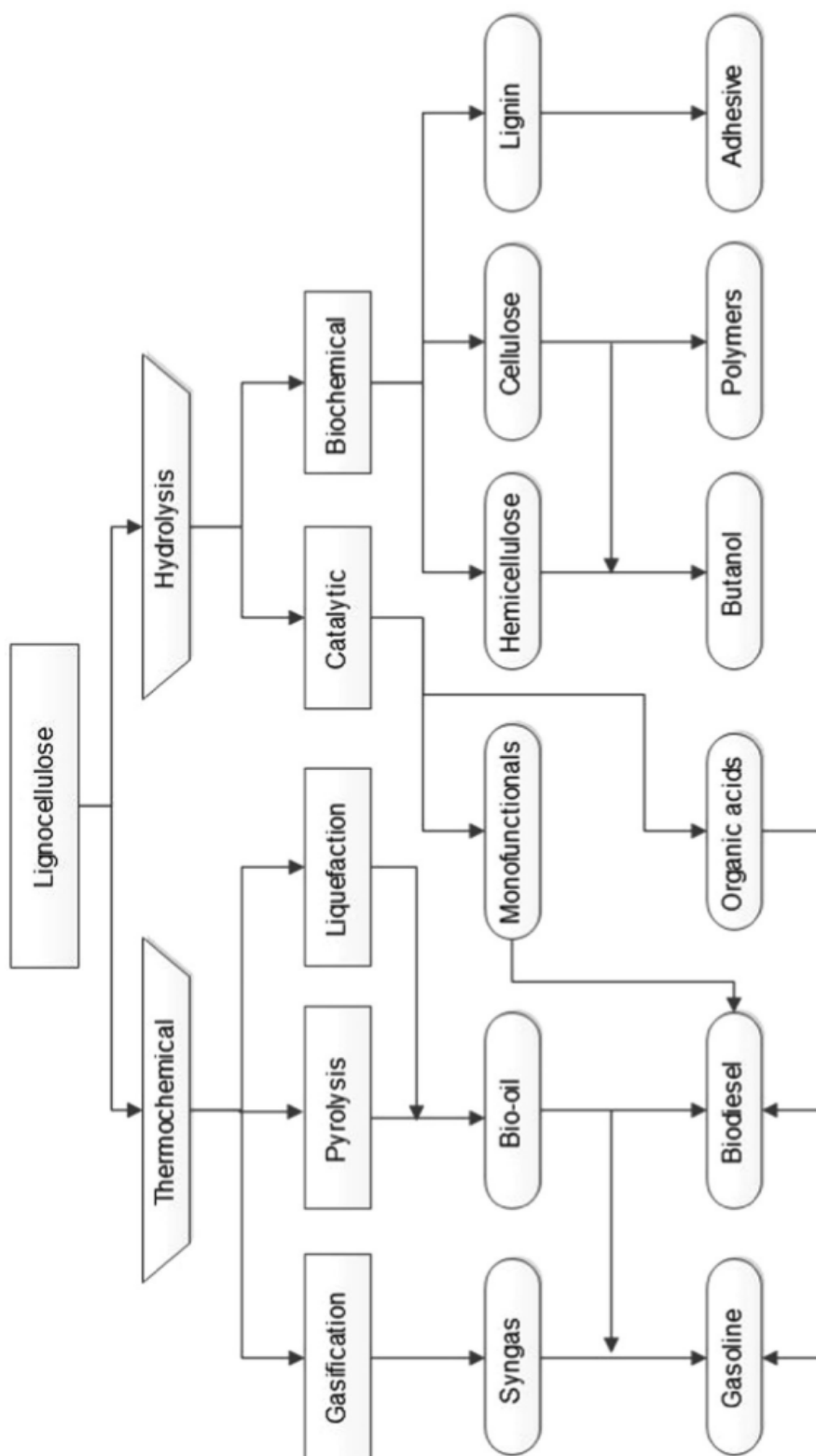


Figure 1.2: Routes and products of thermochemical and hydrolysis processing of lignocellulose (Bharathiraja *et al.*, 2017)

1.2 Butanol as alternative (bio)fuel

The four carbon alcohol Butanol (n-butanol) is colorless and flammable substance, largely produced by the petrochemical industry and used primarily as solvent. There has been a lot of discussion about its use as alternative fuel due to its properties similar to gasoline, but with better performance when compared to ethanol, the current main alternative biofuel. Butanol is easier to ignite due to its lower heat of vaporization; has higher calorific value, enhancing mileage, and has the advantage of being less corrosive. It can also be used directly, pure or blended, in the current gasoline engines without the need of retrofitting and can be further converted to jet fuel (Bharathiraja *et al.*, 2017; Visioli *et al.*, 2014). A comparison of selected physical properties is given in Table 1.1.

Table 1.1: Selected physical properties of Butanol, Gasoline and Ethanol

Properties	Butanol	Gasoline	Ethanol
Melting point (°C)	-89.3	-57.1 to -56.6	-144
Specific gravity	0.810-0.812	0.713	0.79
Ignition temperature (°C)	35-37	422.7	276-456
Energy content (BTU/gal)	110,000	115,000	84,000
Heat of vaporization (MJ/kg)	0.43	0.36	0.92
Research Octane Number (RON)	96	91-99	129

Other butanol isomers —isobutanol and tert-butanol —can be used as gasoline additives and octane boosters, but n-butanol has the highest degree of miscibility with gasoline. There is also an expectation of blending with diesel, that could take advantage of its higher oxygen content to reduce emissions. As in everything, some disadvantages also exist. Ethanol is expected to deliver better efficiency, because it has a higher octane number. In this regard, a modification on the engine would be necessary to keep the same level of efficiency. This relates to greenhouse gas emissions as well, because a lower compression ratio would have to be used, increasing the formation of these gases (da Silva Trindade and dos Santos, 2017).

As previously stated, the interest in renewable and sustainable fuels,

commonly known as biofuels, has been increasing due to the environmental challenges humanity is currently facing. Numerous governmental incentives have come up for research and development for biofuels, renewing the interest in the biochemical route for butanol production.

1.2.1 Butanol Production and the ABE Process

Butanol was obtained in its early days by fermentation, as was ethanol. However, in the 1950s the petroleum route became much more competitive due to oil low prices. A mixture of n-butanol and iso-butanol is obtained through the oxo-alcohol process, a catalytic reaction of propene in the presence of CO and hydrogen. There is, however, an important aspect of feedstock cost, as propene is a commodity and its price is directly related to the one of crude oil. Moreover, propene is raw material for other products, most notably polypropylene, generating a competition related to prices and market demand. Nevertheless, this remains until today the main economically viable production process for butanol (Visioli *et al.*, 2014).

The original fermentation process for butanol production is the so-called ABE fermentation process (Acetone, Butanol and Ethanol), developed in 1916 using the bacteria *Clostridium acetobutylicum* to ferment a starch-rich substrate (such as potatoes). As the name states, the main fermentation products are Acetone, Butanol and Ethanol, obtained in a ratio of 3/6/1 (in volume), all of which find numerous industrial applications, including as fuel. This process was well described and discussed in previous thesis in the SuPER group.

In the current state of art of the ABE process, several different substrates and strains from the *Clostridium* family can be employed for fermentation. From the substrate side, the main concern is the availability and economic feasibility of biomass. Currently, agricultural wastes, cellulosic biomass and lignocellulosic biomass have been under the focus, because they do not compete with food production and are, currently, inexpensive. (Bharathiraja

et al., 2017; Xue *et al.*, 2014). The selection of substrate determines the necessary processes in the upstream section, where biomass is prepared for fermentation. While most biomasses require hydrolysis and detoxification, lignocellulosic substrates require an additional step called pretreatment. Several physical, physico-chemical, chemical and biological pretreatment techniques have been discussed in the literature, with steam explosion and acid or basic treatment being cited as cost-effective. For hydrolysis, main technologies involve acid or enzymatic routes (Li *et al.*, 2019).

From microorganism side, the main concern is the high toxicity of butanol, reason why the butanol yield in the fermented broth, and consequently the other components, is low. As an average, a concentration of 20 g/L is the limit for inhibition of microbial growth (Visioli *et al.*, 2014).

Numerous research studies have been dedicated to the economic feasibility of the ABE process from the product yield point of view. This includes, not limited to, use of genetically modified microorganisms and reactor research to migrate from batch to continuous process, which is challenging due to the anaerobe nature of *Clostridium* species. This is the midstream section of the process, where the biomass broth is fermented. Strain development alternatives include metabolic engineering, random mutagenesis, screening of natural strains and synthetic biology. From reactor point of view, batch reactors are suitable for research and small scale production, while efforts have been made to develop advanced fed-batch and continuous midstream sections to increase yield (Li *et al.*, 2019).

1.2.2 Biobutanol production challenges

One of the main challenges for the production of chemicals and fuels from biomass, butanol included, is the availability and cost of raw materials. In fact, these products compete in the same market as the ones produced from oil feed stocks, rendering the cost of raw materials an important competitiveness factor, apart from process technology and efficiency. With current agricultural

practices and the supply chain involved, prices of crops such as corn or soy bean are influenced directly by the prices of oil. However, as commodities, they follow their particular prices trend. The real game changer is the use of second generation crops, as mentioned in section 1.1, that provide an abundant source of biomass without competition with food production. Lignocellulosic biomass is the fourth largest energy source in the world; relatively inexpensive compared to other crops; and its use contributes in the reduction of waste disposal and greenhouse gas emission problems. Another source of second generation crops is the aquaculture, that can supply algal biomass. Eventually, with multiple and renewable sources available, biomass feedstock can become more competitive than oil, causing biorefineries to overtake as the main source for chemicals (Yang and Yu, 2013).

Also in this regard, the biomass feed stock poses an additional challenge regarding the seasonality of the crops. In fact, supply can vary considerably within a year due to weather and other phenomena in the natural cycle of the plants. It translates in a particular biomass being available during a particular time, such as residues of corn, that is available from September to November in the northern hemisphere. Other biomasses such as wood residues may be available all year round, but yield may change from month to month. On the other hand, there is a continuous demand for chemicals and, particularly, fuel for transportation. Therefore, when using biomass as raw materials, storage and supply chain management are key factors to ensure continuous operation of biorefineries (Yue *et al.*, 2014).

Another major challenge for butanol production, in particular, is the separation process and its efficiency. The downstream section of the process is where the fermentation products are recovered from the broth. Since the increase in concentration of butanol during the solventogenic phase, when microorganisms eventually convert intermediate substances into the desired products, inhibits further production due to its toxicity, efforts have been made to continuously separate products from the broth. This technique is called *in situ* product recovery (ISPR), because it generates a more concen-

trated ABE mixture, while allowing the fermentation process to continue, ultimately reducing the generated waste. It presents an important challenge in terms of energy due to the low concentration of products and, consequently, the high amount of water that needs to be initially separated from the other components. For this reason, the use of distillation as separation technique at this point of the process is not economically feasible. In fact, separating butanol directly after fermentation by distillation can consume more than 2 times the actual energy content of the product, in practice rendering the process infeasible (Patraşcu *et al.*, 2017).

When the objective is to produce butanol via the ABE process, it is of vital importance to increase the separation yield with respect to this product. Several other technologies were proposed and studied for the first separation of ABE and water (Abdehagh *et al.*, 2014). Adsorption is carried out by a suitable adsorbent, usually resins or zeolites, from which the components are subsequently desorbed by change in temperature and/or using displacers. It is of paramount importance to use high selectivity adsorbent with respect to butanol, due to the large amount of other components (ABE, but also other low concentration metabolic products from fermentation) in the broth.

Gas stripping consists in passing gases (oxygen free nitrogen or fermentation gases) through the fermentation broth, that strip ABE from the mixture to near equilibrium conditions. Then the gases are condensed, separating ABE from depleted gas, that is recycled to the fermenter. It is a relatively simple technique that can be applied continuously to the fermenter because it does not damage the microorganism, leading to higher productivity and yield.

Liquid-liquid extraction (LLE) is a process where an extractant —usually an organic solvent —is mixed with the fermentation broth to remove the products of interest. It is important that the organic phase is immiscible with water, allowing it to be easily separated. An organic solvent that dissolves preferentially butanol is desired, in the case that it is the product of interest; at the same time, it cannot be toxic to the microorganisms, and must have

low interaction with components that impact the fermentation process.

Pervaporation is a separation technology where a liquid mixture is separated by partial vaporization through a membrane. Liquid feed is in direct contact with one side of a hydrophobic membrane, while vacuum or a gas flowing create a depression on the permeate side, allowing the permeate to be removed as vapor, later condensed to recover the products of interest. In this process, the heat of vaporization for separation is provided by the feed itself, making it very competitive. Other technologies that are researched include extraction, perstraction, reverse osmosis and hybrid techniques.

These processes were well discussed in the work of Boffa, where pros and cons of each were taken in consideration. Eventually, the liquid-liquid extraction was chosen as separation technique to be studied, due to the availability of experimental data (Boffa, 2015). An illustration of the energy requirement of different butanol separation processes is given in Figure 1.3 (Qureshi *et al.*, 2005).

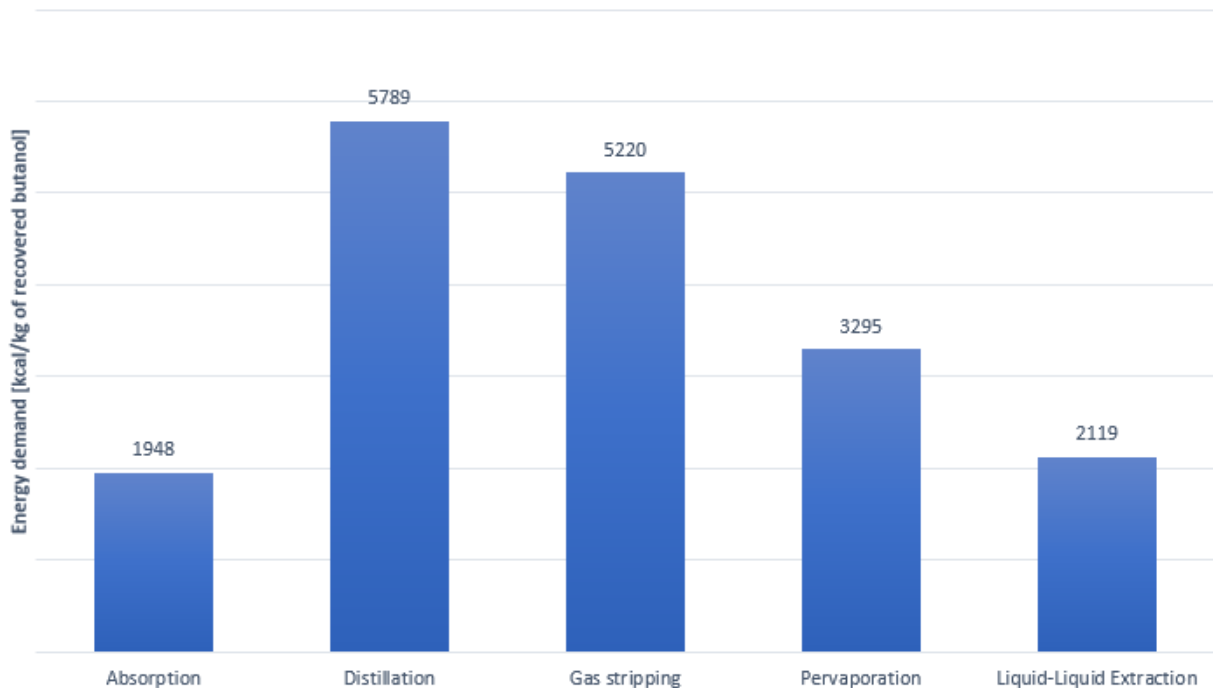


Figure 1.3: Energy demand of various processes for separating butano from ABE fermentation broth

Many of the technologies mentioned above are yet in research and development phase, still subjected to industrial scale up. Distillation, on the other hand, is an old, proven technology, widely applied and with solid technological basis. Therefore, the workaround to this problem is the combination of ISPR techniques with distillation, that can dramatically reduce the costs of butanol recovery. If fermentation could result in a butanol concentration of 4 wt%, the ratio of energy demand with respect to the energy content of butanol would decrease to 0.25.

Following the work of Boffa, di Pretoro focused on the dynamic simulation of the purification section of an ABE plant. This study further discussed the distillation train after the dewatering section (liquid-liquid extraction), giving an overview of involved costs in the operation (di Pretoro, 2017). The purification was composed of three distillation columns, of which acetone and butanol were recovered as pure (98% and 99%, respectively) products, because they are the most valuable ones. Two other streams containing azeotropes are also obtained. While the ethanol-rich stream (containing also water and traces of acetone and butanol) is considered as waste, the water-butanol stream can be further separated to increase the butanol recovery of the plant.

1.3 Scope of the work

The present Master of Science thesis dedicated to the detailed investigation of the separation of a water-butanol azeotrope stream by distillation, originated from the distillation train of ABE. It completes the study on the purification scheme of a ABE plant, giving information on the recovery of an additional fraction of one of the products of interest that otherwise would be lost, increasing the efficiency of the complex. It is the continuation of previous works on the topic: two other thesis developed in the SuPER group by Eng. A. di Pretoro, on the Dynamic simulation and plant-wide control of an ABE/W separation plant, and A. Boffa, on the analysis and optimization of the purification scheme of ABE fermentation. None of the two investigated

in detail the azeotropic distillation section.

Chapter 2

Distillation of Azeotropes

2.1 Distillation and the Vapor-Liquid Equilibrium

Distillation is by far the most important separation process in the chemical industry. It has been used for many years —even before its bases as unit operation were set —commonly to concentrate alcoholic content of beverages. The first distillation still vertical and column-shaped dates back to 1813, developed by Cellier-Blumenthal, in France, while the first book on the fundamentals of distillation was written by Ernest Sorel, and released in 1893. In the beginning of the twentieth century, distillation was recognized as key tool to separate crude oil into its different cuts, starting its story of success among the chemical processes.

The operation consists in physically separating a liquid mixture into two or more products by successive evaporation and condensation in stages in a column, where liquid is flowing downwards and vapor is flowing upwards. Basically, it relies on the fact that the vapor phase is richer in the more volatile components with respect to the liquid phase; this statement is a simple approach to the vapor-liquid equilibrium (VLE). In a conventional distillation operation, energy required for the separation is added to the column at the bottom through the reboiler (point of highest temperature). Heat is removed from the top through the condenser (lowest temperature).

Figure 2.1 illustrates a standard distillation column. It is a process that requires large amounts of energy and presents low overall thermodynamic efficiency, which in turn opens a number of possibilities for optimization and integration (Green and Perry, 2007).

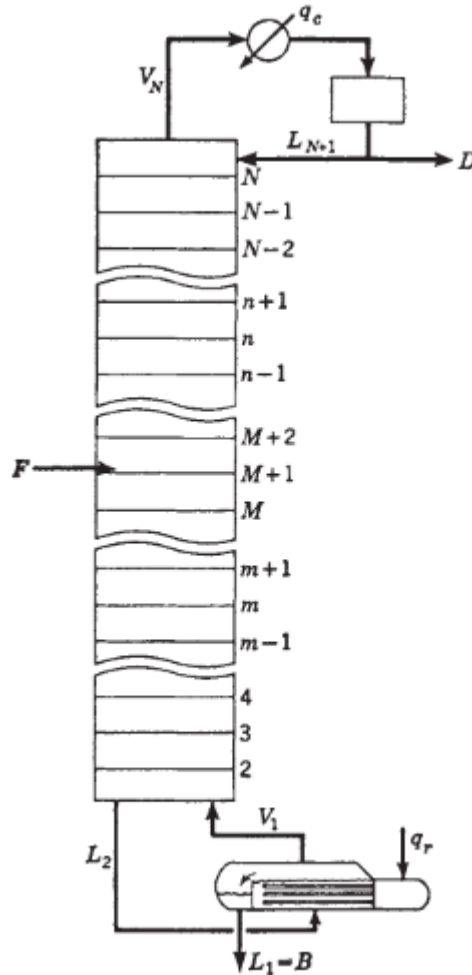


Figure 2.1: Standard distillation column, showing the internal flows of vapor and liquid. (Green and Perry, 2007)

In fact, the inside of a distillation column is a complex interplay of the thermodynamic properties of the mixture, heat and mass transfer phenomena and multi-phase flow. The assumption that liquid in each stage is perfectly mixed so that both phases leaving the stage are in equilibrium with each other is what allows the use of VLE to predict the changes in composition through the column. Eventually, the whole process can be designed based on

equilibrium stages to provide a specified purity of top and bottom streams (or recovery of a product). This design differs from actual column results because of inefficiencies associated to the real trays and the column hydrodynamics. However, VLE and thermodynamic data remain the basis to understand and evaluate any separation by distillation.

Distillation is a near isobaric process. It means that, despite the pressure profile inside the column, the whole process can be considered at a fixed pressure. For this reason, experimental data usually is measured over a range of temperature for a fixed pressure (or a set of pressures). The most common representation of VLE data is the vapor-liquid equilibrium ratio, known as the K-value:

$$K_i = \frac{y_i}{x_i} \quad (2.1.1)$$

where i is the component, y is the vapor fraction and x the liquid fraction. The K value is a measure of the tendency of component i to vaporize (H. Kister, 1992). This means that if K is high, the component tends to be present in higher concentration in the vapor phase; if low, in the liquid phase.

The relative volatility α can be defined as the ratio between the K-value of component i over another component of the mixture, say j :

$$\alpha_{ij} = \frac{K_i}{K_j} \quad (2.1.2)$$

For multi-component mixtures (three or more), the relative volatility indicates which component is easier to separate by distillation with respect to the others. By convention, α is defined with respect to the less-volatile component (lower K). If α is high, separation by distillation is easy because one component has much greater tendency to concentrate in the vapor phase. On the contrary, if it approaches unit, separation by distillation becomes increasingly difficult. If $\alpha = 1$, the separation becomes impossible, because the two components behave equally.

The VLE data is frequently presented in the form of x-y Diagrams, a graphic containing the vapor and liquid mole fractions of one of the compo-

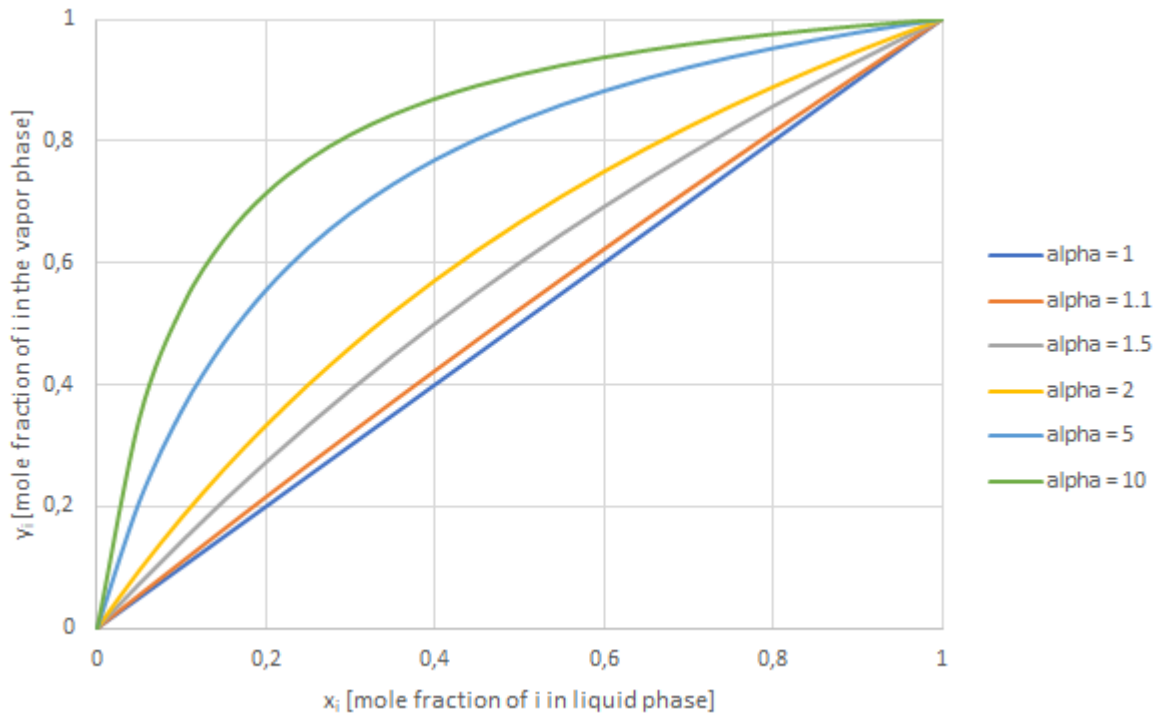


Figure 2.2: x-y Diagram for generic components i and j for different relative volatility (α) values.

nents, with a line of 45° slope for reference (isocomposition line, $\alpha = 1$). The VLE curve depends on the system and the interaction between the molecules. If the mixture is binary, equations 2.1.1 and 2.1.2 can be combined to write y as function of x and the relative volatility (equation 2.1.3):

$$y_i = \frac{\alpha_{ij}x_i}{1 + (\alpha_{ij} - 1)x_i} \quad (2.1.3)$$

Equation 2.1.3 is plotted in figure 2.2 for different values of α . As previously described, the higher the relative volatility, the more the component accumulates in the vapor phase, as can be noticed in the various curves of the diagram. In large scale, distillation is rarely applied if $\alpha < 1.05$.

2.1.1 Determination of liquid and vapor compositions of VLE

Being the K-value the ratio of liquid and vapor composition of a species, it is also a function of temperature, pressure and VLE. For mixtures of compounds and conditions that can be described by the ideal gas law, the determination of the K-value is straightforward by the application of Dalton's and Raoult's laws, that relate the component partial pressure to the vapor composition and the liquid composition, respectively (equations 2.1.4 and 2.1.5):

$$P_i = y_i P \quad (2.1.4)$$

$$P_i = x_i P_i^{sat} \quad (2.1.5)$$

From these relations the K-value can be simply determined making explicit x and y as follows:

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{sat}}{P} \quad (2.1.6)$$

When the components behavior cannot be described by the ideal gas law, the non-idealities of vapor and liquid phase need to be correctly described to allow for useful calculations. In these cases, the K-value must be written as function of the component's fugacity coefficients for vapor and liquid phases (equation 2.1.10).

More generally, when the phases in a system are in equilibrium, the vapor fugacity f_i^V is equal to the liquid fugacity f_i^L :

$$f_i^V = f_i^L \quad (2.1.7)$$

Simplifying the thermodynamic concept, the fugacity can be regarded as corrected versions of partial pressure for vapor (equation 2.1.8) and liquid (equation 2.1.9). The correction factor is called fugacity coefficient, represented by the greek letter Φ (capital phi).

$$f_i^V = \hat{\Phi}_i^V y_i P \quad (2.1.8)$$

$$f_i^L = \hat{\Phi}_i^L x_i P \quad (2.1.9)$$

$$K_i = \frac{\hat{\Phi}_i^L}{\hat{\Phi}_i^V} \quad (2.1.10)$$

When the fugacity coefficient is equal to 1, the result is the same as the ideal case. To calculate analytically the fugacity coefficients, P - V - T expressions—Equations of state—are used, of which the most common are the cubic equations of Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK).

The liquid phase can also be described by a different approach, where the fugacity of the component is related to the composition through the activity coefficient γ (gamma). This coefficient is function of the activity (a) of the component in the liquid phase and to a standard-state fugacity (f^o):

$$\gamma_i \equiv \frac{a_i}{x_i} = \frac{f_i^L}{x_i f_i^o} \quad (2.1.11)$$

The determination of the activity coefficient is not straightforward, and the full concept and derivation are object of several thermodynamics texts (see Prausnitz *et al.*, 2000). In essence, the activity coefficient can be obtained from the excess Gibbs energy (G^E), i.e. the observed Gibbs energy of a mixture when compared to expected values of an ideal solution at the same temperature, pressure and composition. Starting from this concept, individual activity coefficients can be derived by applying the Gibbs-Duhem equation.

Therefore, the computation of the excess Gibbs energy is essential to the calculation of VLE through the activity approach. Several expressions have been proposed that allow to calculate G^E as function of composition. These are the so-called activity models, mathematical expressions with two or more binary, adjustable parameters, that relate experimental vapor-liquid equilibrium data. The choice of the activity model will depend on the nature of the components of the mixture, some being more useful than others, considering the adjustment to experimental data and the mathematical complexity of the model. Equations such as Margules and van Laar are among the older models, while others such as Wilson, Nonrandom Two Liquid (NRTL) and Universal QuasiChemical (UNIQUAC) are newer and more suited to a broader range of substances, including polar ones.

2.2 Azeotropic mixtures

For some of those mixtures, one component can be more volatile than the other over the entire analyzed range, as exemplified in x-y diagram of figure 2.2. This is the case of the mixture benzene-toluene for example, exhaustively described in the chemical engineering literature (J. Douglas and M. Douglas, 1988). For another type of mixtures, usually when there's a strong physical or chemical interaction between the species, one of the components is more volatile over only a part of the range, generating a curve with inflection point, after which the volatility is reversed. These are the so-called azeotropic mixtures. The composition of the inflection point, in which vapor and liquid fractions are equal, is called azeotrope or azeotropic composition.

The azeotropes can be divided into homogeneous, when only one liquid phase is formed, in equilibrium with one vapor phase; and heterogeneous, when two or more liquid phases are formed, also in equilibrium with one vapor phase. Moreover, they can be classified as minimum-boiling azeotrope if it boils at lower temperature than either of the pure components; maximum-boiling temperature if it boils at higher temperature.

Essentially, azeotropes are non-ideal systems that exhibit a sufficient, positive or negative deviation from Raoult's Law, depending on the activity coefficient, leading to maximum ($\gamma_i < 1$) or minimum-boiling ($\gamma_i > 1$) behavior. When the deviation is small, the system is considered a nearly ideal mixture, which can still form an azeotrope if the vapor pressure curves of the component intersect (known as Bancroft point). To allow for liquid-liquid phase separations, deviations from Raoult's Law must be strong and positive; therefore, maximum-boiling azeotropes are always homogeneous.

Some examples of azeotropes are given in Figures 2.3 to 2.6. They are the x-y and T-x-y diagrams of the mixtures Ethyl Acetate-Ethanol, a minimum boiling azeotrope, and Chloroform-Acetone, a maximum boiling azeotrope. From x-y diagrams it is possible to notice the inversion the the volatility of the

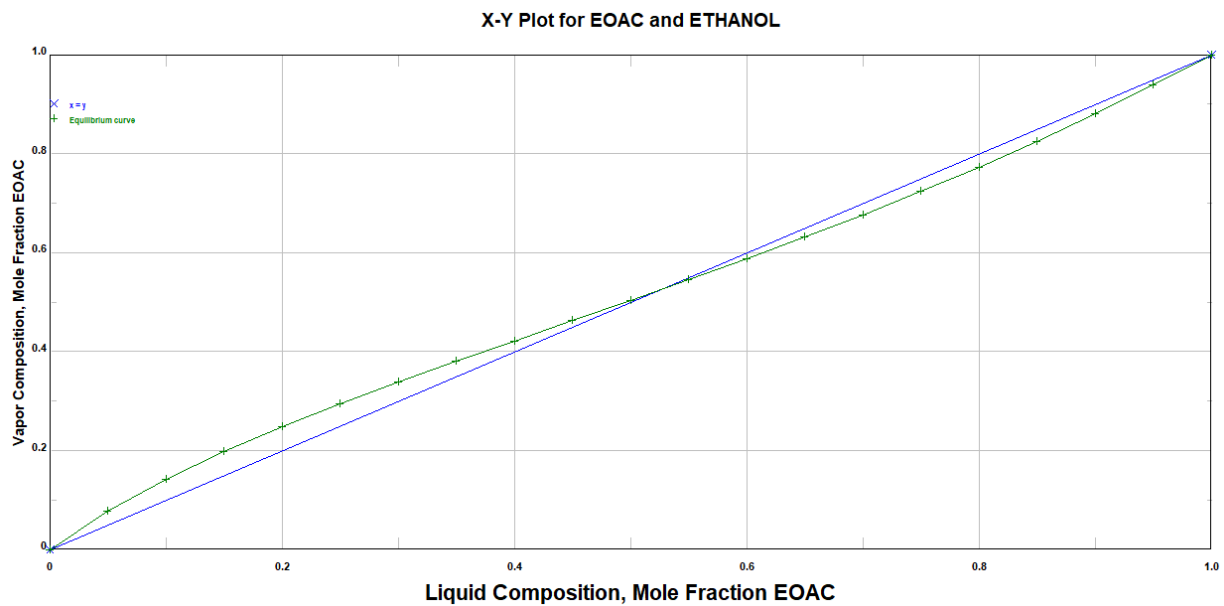


Figure 2.3: x-y Diagram for VLE of Ethyl Acetate-Ethanol mixture at 1 kgf/cm^2 (101.3 kPa) using Soave-Redlich-Kowng Equation of State.

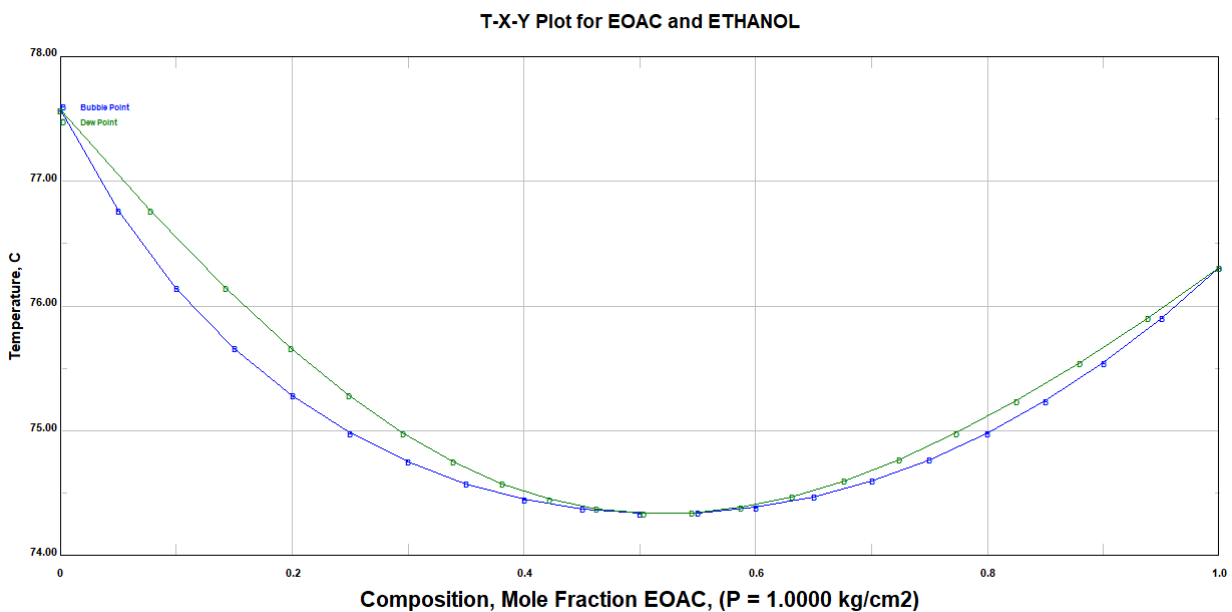


Figure 2.4: T-x-y Diagram for minimum boiling azeotrope mixture of Ethyl Acetate-Ethanol at 1 kgf/cm^2 (101.3 kPa).

components, while the T-x-y diagram shows the bubble and dew temperatures with respect to one component of the mixture. From the latter it is clear that when the composition approached the minimum or maximum boiling point,

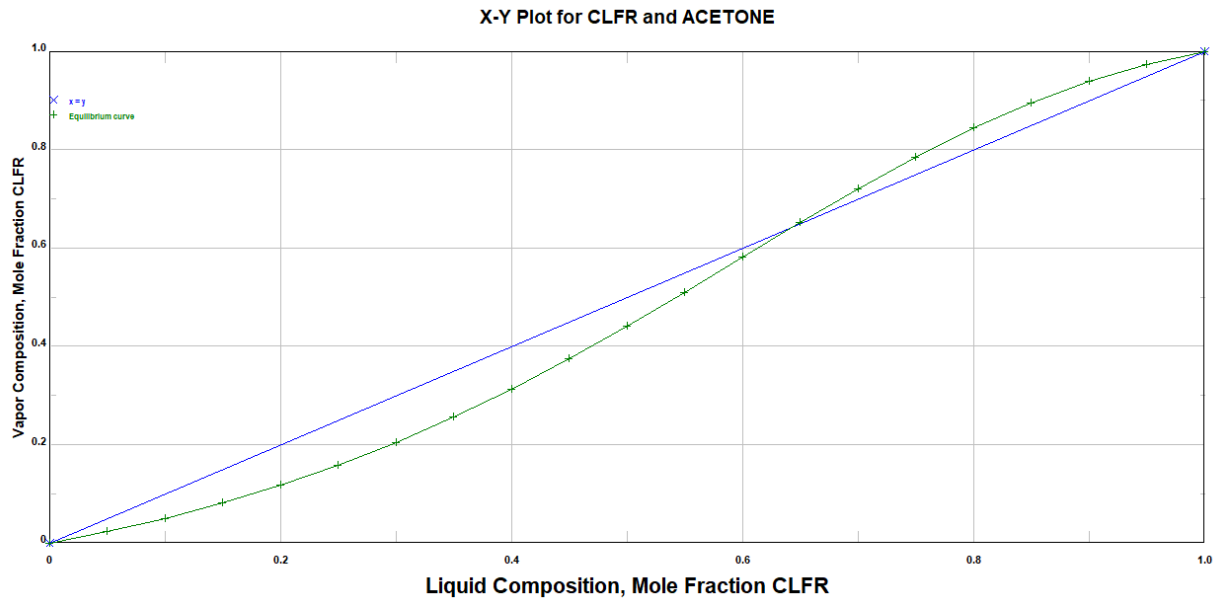


Figure 2.5: x-y Diagram for VLE of Chloroform-Acetone mixture at 1 kgf/cm^2 (101.3 kPa) using NRTL activity model and ideal gas law.

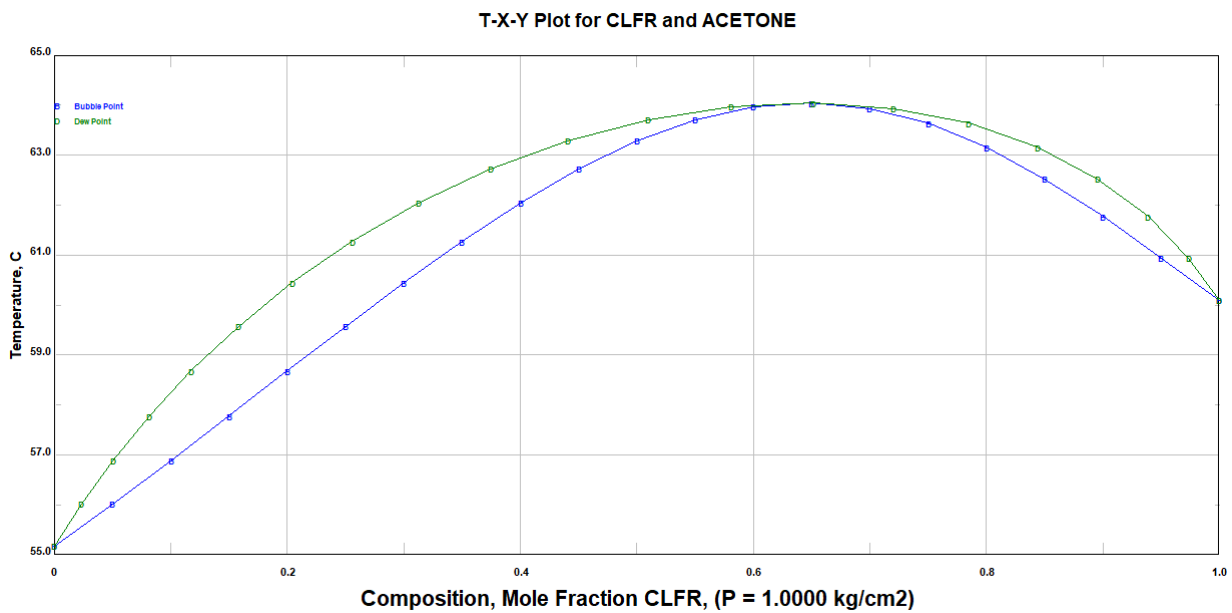


Figure 2.6: T-x-y Diagram for maximum boiling azeotrope mixture of Chloroform-Acetone at 1 kgf/cm^2 (101.3 kPa).

no distinction between phases is possible. The VLE graphics were generated in the PRO/II simulator with adequate thermodynamic packages for each mixture.

2.3 Azeotropic distillation

In practice, once the azeotropic composition is reached, a mixture cannot be separated further. If it is a minimum-boiling azeotrope, it exits the column at the top (lowest temperature in the column); if it is a maximum-boiling azeotrope, leaves at the bottom. Therefore, additional processes must be applied to further separate azeotropes into higher purity components.

Azeotropic distillation is the term that is used to indicate different techniques based on distillation to separate azeotropes. Generically, these processes exploit the behavior of azeotropic mixtures when subjected to a third agent, called *entrainer*, that may be added to the feed or be already present (self-entraining). The entrainer has the role of forming a more favorable azeotrope by changing the VLE of the mixture, allowing the recovery of components in higher purity degrees by the use of sequential standard distillation columns. The entrainer is then recovered in one of the columns and recycled to the start of the process. Sometimes the (selected) entrainer may lead to phase-splitting, with liquid-liquid immiscibility. In such cases the process becomes more versatile, as physical separation processes, such as decantation or membranes, may also be used.

Extractive distillation, sometimes synonym to azeotropic distillation, can be distinguished by the fact that the entrainer joins the column not with the feed, but at a different tray. It creates, in practice, a different section in the column, where the interaction of the mixture with the entrainer promotes a shift in the composition by extraction. This way the rectifying and the stripping liquid profiles are connected, creating a sort of a bridge between the sections, that allows to obtain a pure product where sometimes a traditional azeotropic distillation would be unfeasible (Gorak and Olujić, 2014).

Pressure-swing distillation is another alternative for azeotrope separation. It involves no entrainer, but exploits the variation in azeotropic composition with pressure. When compared to extractive or azeotropic distillation, the

process can be more interesting from economic point of view due to the lack of compression costs; it is, however, more difficult to achieve higher purity levels. When the azeotropic composition changes considerably with pressure, two columns operating at different pressures can be used to break the azeotrope into pure products. The mixture acetone-methanol is an example of system where both extractive distillation and pressure-swing distillation can be applied. In this case, process integration and optimization can play a significant role into capital cost determination and process choice (Luyben, 2008b).

Recent studies have pointed ionic liquids as interesting entrainers for azeotropic separation. They are chemically stable salts, liquid at room temperature, non-volatile and non-flammable. These properties turn them into potential alternatives, many times also environmentally friendly ones, because of their strong ability to break azeotropes. It allows their use not only as entrainers for extractive distillation, but also in liquid-liquid extraction. Ionic liquids can also be tailored by the variation of the structure and combination of the ions that compose the mixture, altering properties such as viscosity, selectivity and chemical stability. (Pereiro *et al.*, 2012).

Finally, a relatively novel distillation technique known as dividing wall column (DWC) is also being studied for separation of azeotropes. It consists in a combination of two or more columns into just one “shell”; feed enters the column and an internal wall divides the shell into distinct sections, where different separations take place. Eventually, products are recovered not only from top and bottom, but also through side draws, depending on the number of walls and their position. Figure 2.7 shows a schematic example of DWC. Due to the high number of degrees of freedom, only recently with the development of computer aided modeling and simulation these equipment are being studied in depth. DWCs can be used to separate multicomponent mixtures, as well as azeotropic, particularly by combination with entrainers that form heterogeneous azeotropes. Applied processes are, however, still scarce. (Yildirim *et al.*, 2011).

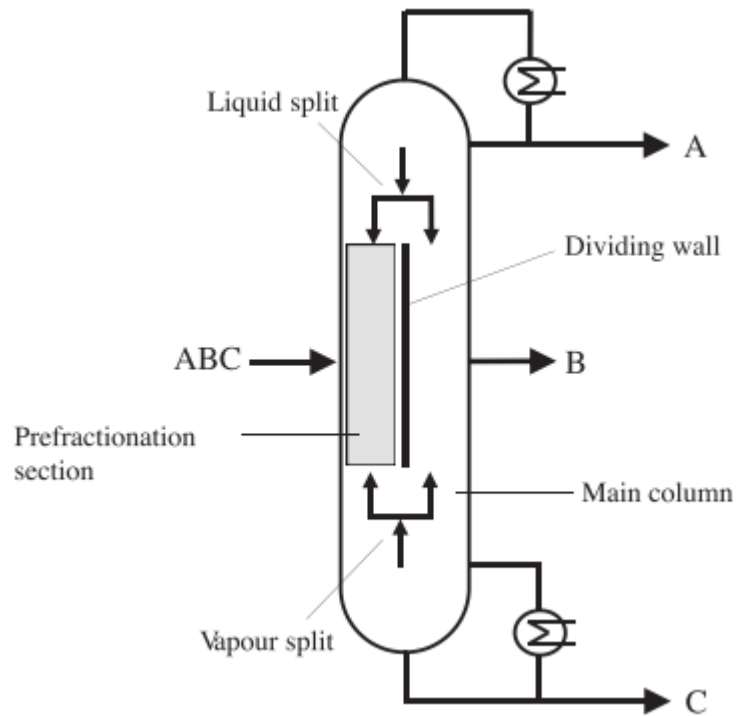


Figure 2.7: Schematic concept of a Dividing Wall Column. (Yildirim *et al.*, 2011)

The phase equilibrium and distillation process of the water-butanol mixture will be described in more detail in the next chapter.

Chapter 3

Separation process of water and butanol

The simulation of distillation columns is complex from computational point of view, particularly for non-binary and non-ideal mixtures. When it comes to azeotropic distillation, despite the additional difficulty imposed by these systems, most process simulation software can handle this kind of separation with satisfactory results. Steady-state and dynamic behavior of a process can be determined, provided that the system is thermodynamically well characterized, either by equation-of-state, activity model or both.

3.1 Azeotropic distillation of water – butanol mixture

When mixed, water and butanol form a binary minimum-boiling heterogeneous azeotrope. In this case, butanol serves as self-entrainer, as defined in Chapter 2, because when the azeotrope composition is reached, phase separation occurs and a liquid-liquid equilibrium (LLE) is established. The formation of two liquid phases is a very useful phenomenon to break the azeotrope, because the composition of each of the phase is automatically different from the azeotropic point, and in opposite sides of the equilibrium curve with respect to this point. This means that they can be further processed to increase each component purity. The separation of liquid phases can be performed by simple units, such as a decanter. Sometimes, other

physical processes such as membranes chromatography or adsorption can be used.

The proposed separation scheme for water-butanol mixture is the one established in the previous thesis of SuPER Group about the ABE process. Particularly, Di Pretoro states that the additional butanol recovery from the azeotropic distillation section is relevant, considering also that butanol is the most valuable product obtained from ABE fermentation process. A separation section composed of two distillation columns and a decanter was proposed, as shown in the Process Flow Diagram (PFD) of Figure 3.1. A similar system was studied also by Luyben, 2008a and Patraşcu *et al.*, 2017.

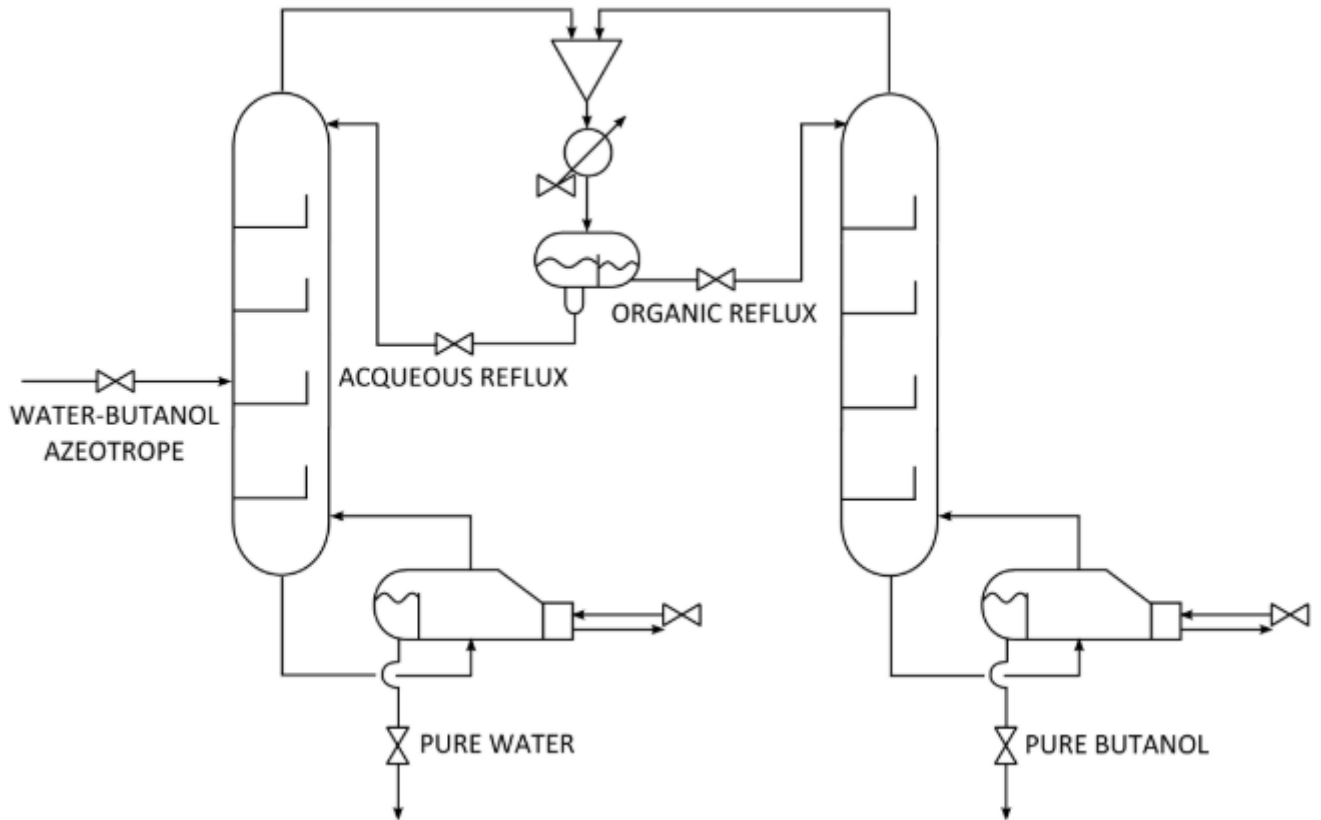


Figure 3.1: Process flow diagram of proposed azeotropic distillation section for water-butanol mixture (di Pretoro, 2017)

3.2 Process description

The water-butanol separation section basically consists of two identical distillation columns - for the sake of simplicity, hereafter named water-column and butanol-column - one condenser and one decanter. The fresh feed is a stream composed of water and butanol, originated from the previous purification processes of an ABE plant. It goes straight into the water-column (first column), which is aimed to obtain a purified water stream at the bottom. Being the mixture a minimum-boiling azeotrope, the top stream is at or very close to the azeotropic composition (lowest temperature in the column); it goes to the condenser, where it is totally condensed. The liquid outlet from the condenser enters the decanter, where phase separation occurs due to the heterogeneous behavior of the mixture. The water-rich liquid phase is pumped back to serve as reflux to the water-column. The butanol-rich phase is pumped to the butanol-column (second), concentrating butanol at the bottom stream.

The overhead of the second distillation column is also close to the azeotropic composition, because butanol is continuously stripped from the vapor phase until the composition is back to the azeotropic one, approaching from the opposite side of the equilibrium curve. Therefore, this stream also goes to the condenser, mixing with the overhead of the first column before the inlet. Since this is a self-entraining system and the entrainer is the product itself, no concerns about recovery are needed.

In particular, the use of a decanter after the condenser at the top of a distillation column for heterogeneous azeotropes is a consolidated approach to increase the efficiency of the separation of such mixtures. The decanter allows the demixing of the components through LLE, while also opening the possibility of changing the composition of the liquid phases by modifications in the overcooling degree. Usually the overcooling is not interesting in distillation columns, because it increases the duty in both the condenser (for the overcooling) and the reboiler (because an overcooled reflux is more distant

to the equilibrium). However, when LLE is relevant and demixing occurs, changing the overcooling degree can have positive effect on the composition of the liquid phases, in such manner that it becomes easier to achieve the required specification (Di Pretoro *et al.*, 2020).

When, by any reason, the feed is richer in butanol than standard conditions, it can enter straight into the butanol-column or directly in the decanter. Since the feed is originated from ABE fermentation, the usual condition is water-rich. Inlet butanol composition can change to higher levels. shifting to the two-liquid region, justifying entering at the decanter.

3.3 Phase equilibrium of water – butanol mixture

To simulate the equipment dealing with water-butanol mixture, it is of paramount importance to describe correctly both the vapor-liquid and liquid-liquid equilibria of the system.

The academic literature is rich in VLE and LLE data for water-butanol systems, because of the continuous interest in this alcohol and the needs to develop processes to its production and transformation. References go as early as Stockhardt and Hull, 1931 and Kato *et al.*, 1970 for pure water-(1-butanol) systems, while more recently ternary mixtures involving water-butanol and other organics as entrainers are being studied for applications such as extraction and enhanced distillations. Examples are the works on VLE and LLE of Zhu *et al.*, 2012 with 3-methyl-1-butanol (isoamyl alcohol); Gomis *et al.*, 2014 with p-xylene; and Garcia-Cano *et al.*, 2018 with 2-octanol. They all have in common the correlation of experimental data with NRTL and UNIQUAC thermodynamic models to obtain binary interaction parameters. Other references are shown in Table 3.1.

The equilibrium of water-butanol in the simulator Pro/II was studied in detail by Boffa, 2015. Activity models NRTL and UNIQUAC were chosen to represent the system because of their proven capacity to describe the

Table 3.1: Selected references on thermodynamic models for mixtures containing water and butanol

Comp. 1	Comp. 2	Comp. 3	VLE Model	LLE Model	References
Water	Butanol	Toluene	NRTL UNIQUAC	NRTL UNIQUAC	Gomis <i>et al.</i> , 2015
Water	Butanol	Isobutanol	NRTL	UNIQUAC	Chen <i>et al.</i> , 2019
Acetone	Butanol	Ethanol	NRTL	NRTL	Van der Merwe <i>et al.</i> , 2013 Errico <i>et al.</i> , 2016 Sánchez-Ramírez <i>et al.</i> , 2017 Patraşcu <i>et al.</i> , 2017
Water	Butanol	Isobutanol	UNIQUAC	UNIQUAC	Gai <i>et al.</i> , 2018
Water	Butanol	Biodiesel	UNIFAC	-	Dumitrescu <i>et al.</i> , 2019
Water	Butanol	-	-	UNIFAC	Boutikos <i>et al.</i> , 2014
Water	Butanol	2-Octanol	NRTL UNIQUAC	NRTL UNIQUAC	García-Cano <i>et al.</i> , 2018
Water	Butanol	Isoamyl Alcohol	-	UNIQUAC	Zhu <i>et al.</i> , 2012
Water	Butanol	-	UNIQUAC	UNIQUAC	Luyben, 2008a

behavior of non ideal mixtures, as well as the amount of data available for this system. The validation of the parameters available in software’s database against experimental data from literature showed that LLE was described satisfactorily by NRTL model, but not by UNIQUAC model. On the other hand, VLE was described properly by both models.

To increase the accuracy of the simulation, it was decided to proceed with experimental data regression to obtain the binary parameters for the NRTL model. The algorithm used for regression is part of the BzzMath library, developed by Buzzi-Ferraris and Manenti, 2012, that allows the solution of “narrow-valley problems”. Eventually, the binary interaction parameters of a five-parameter NRTL model were obtained, for fixed parameter $\alpha = 0.2$ kJ, valid in the temperature interval of 0 to 120°C, at atmospheric pressure. These parameters were used in the simulations that will be detailed in Chapter 4 and are listed in the Table 3.2.

Table 3.2: Parameters of NRTL model for water-butanol system with $\alpha = 0.2[kJ]$, as obtained by Boffa, 2015

a_{ij} [kJ]	Water	Butanol	b_{ij} [kJ]	Water	Butanol
Water	0	13.82	Water	0	-21547.95
Butanol	-4.46	0	Butanol	8350.12	0

As an example, Figure 3.2 shows the T-x-y diagram of water-butanol mixture generated from PRO/II database parameters, and Figure 3.3 shows the data correlation by Boffa.

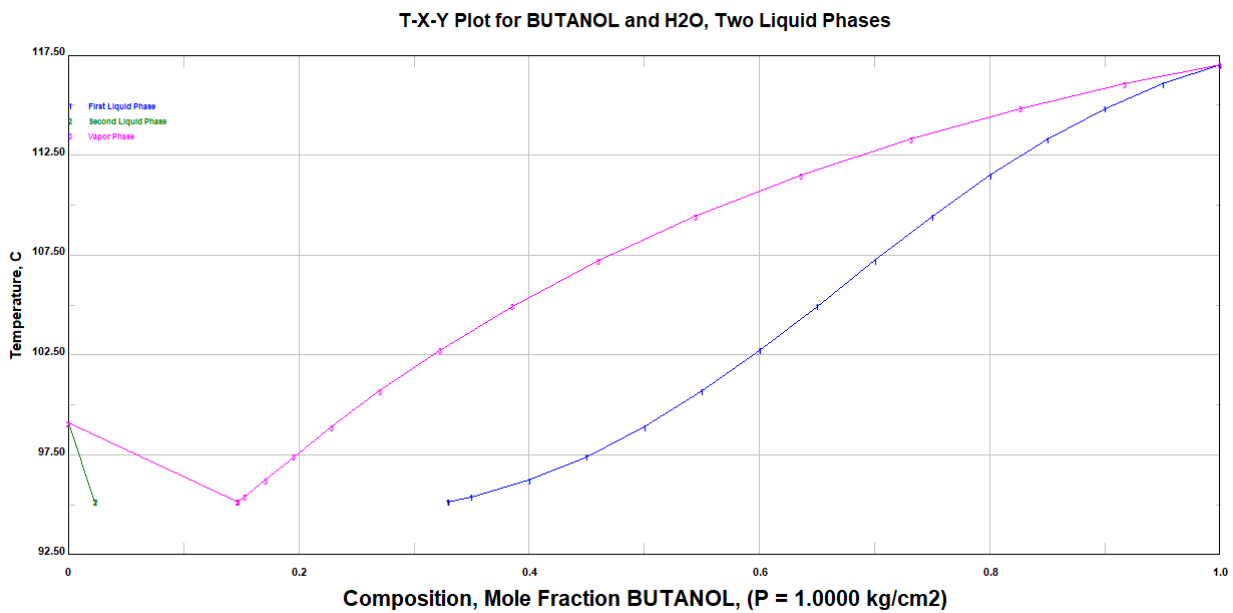


Figure 3.2: T-x-y Diagram of water-butanol mixture as obtained from standard NRTL parameters of PRO/II simulator

3.4 Equipment control philosophy

The main and first objective of a control system is to ensure stable operation. With distillation columns it is not different, because instability can affect the column capacity, cost of operation (OPEX) and products' purity, among others, not to mention safety concerns. Disturbances that arrive or leave the distillation process can be amplified and carried over to different equipment.

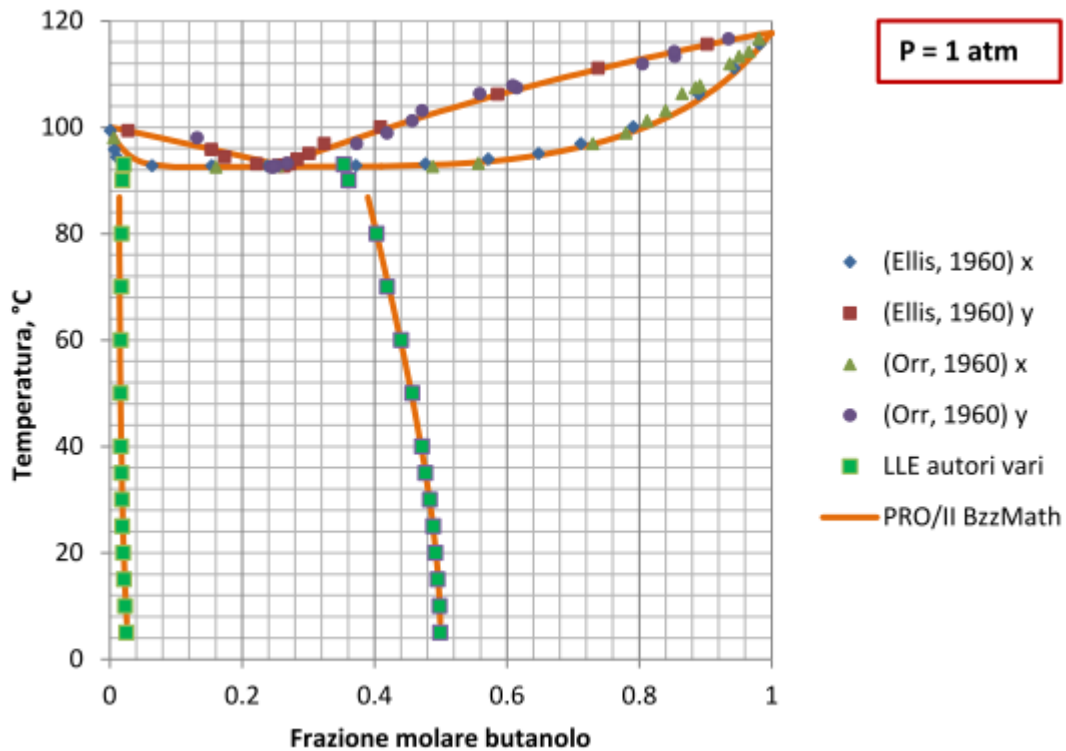


Figure 3.3: Experimental and regression data of water-butanol VLLE, as obtained by Boffa, 2015

The dynamic behavior of distillation columns is straightforward, from a modeling point of view. For a binary system, with constant relative volatility and 100% tray efficiency, the mass balance for each theoretical equilibrium stage i is basically governed by the composition, as shown in Equation 3.4.1:

$$M_i \frac{dx_i}{dt} \equiv M_i x_i = Lx_{i+1} + Vy_{i-1} - Lx_i - Vy_i \quad (3.4.1)$$

The liquid and vapor compositions can be obtained from already mentioned Equation 2.1.3, a function of relative volatility. These two equations form a set of Differential Algebraic Equations (DAE), which is simple to solve with computers. However, the main problem resides on the non-linearity of VLE relations, making the response also strongly non linear.

Despite this difficulty, most distillation columns, even those with high number of stages, can be adequately described by a first-order model with a very large time constant τ . The reason is that, essentially, all trays present the same composition response, because of the interaction among them (Skogestad and Morari, 1988).

The principle objectives of a column control system are:

1. Stable operating conditions
2. Regulation for production in specification (rate and composition)
3. Optimize the column's efficiency (in terms of separation, energy consumption, etc)

For a typical distillation column, excluding flows, there are five variables that are controlled. They are: column pressure; column sump level; condenser or condensate drum level; top composition; and bottom composition. The first three are directly related to stable conditions, while the last two are related to product specification.

For this typical column, the manipulated streams are also in the number of five: top flow rate; bottom flow rate; condensation rate; boilup rate; and reflux flow rate.

Therefore, if each controlled variable needs to be paired with one manipulated variable, there are theoretically 120 possible combinations to control the column. In practice, only some of them are commonly used (H. Z. Kister, 1990).

In the case of the proposed azeotropic distillation system, composition control of the top streams of both columns is not necessary, because they are at or near the azeotrope, which is known. Therefore, only the composition of the bottom streams needs to be controlled, via temperature of bottom of the column as process variable and steam to the reboilers as manipulated

variable. This is also an advantage from control stability point of view, since it avoids problems with coupling of top and bottom compositions.

Since this system uses a total condenser, pressure on condenser or condensate drum is not necessary. Instead, a relief valve can be provided. Temperature can be controlled by regulating the flow of coolant to the condenser, which also allows to overcool the condensate, if desired. On the condensate drum, since there are two liquid phases, two level controls are needed, which are regulated via the reflux stream to each of the columns.

Finally, pressure of the columns is controlled using a regulation valve on each of the top stream, while the feed to the system is simply flow controlled and the sump in both columns can be controlled by regulating bottom stream flow rate. Figure 3.4 represents the control scheme proposed.

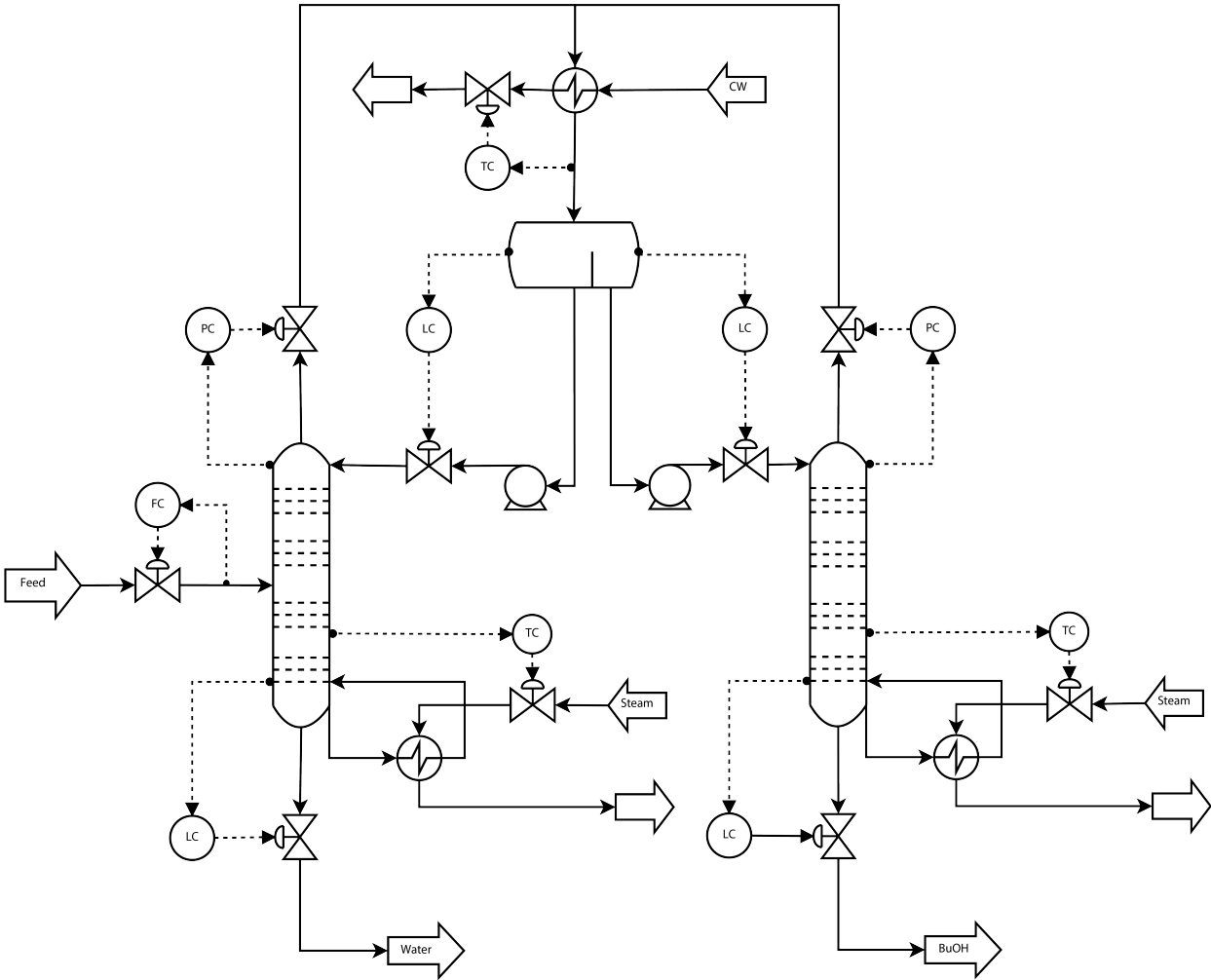


Figure 3.4: Proposed azeotropic distillation control strategy

Chapter 4

Process Simulation

Computer simulation of processes is now a staple resource of the modern chemical engineer. It is used to guide the design of new plants and processes, as well as to troubleshoot and debottleneck existing ones. Recently, important advances were made in the dynamic simulation as well, allowing detailed engineering studies and operator training based on rigorous first-principles models. Moreover, simulators allow processes optimization based on real plant data, to maximize profit and ensure safe operation, for instance. With the development of computers and networks, real time on-line optimization based on Digital Twins and Big Data has been rapidly generating improvements in the chemical industry as a whole.

Simulation is of particular importance for distillation, because of the high number of balance equations involved and the complexity of calculations. A successful simulation requires the following steps:

- Definition of modeling equations
- Thermodynamic properties data and calculations
- Analysis of the degrees-of-freedom
- Solution of the systems of equations

The traditional approach for solving distillation problems is the equilibrium-stage model, that considers that vapor and liquid from previous stages and any possible feed stream arrive at a stage; the vapor and liquid phases that leave this stage are in equilibrium with each other. Then, the complete process is modeled a succession of stages, as represented in Figure 4.1. The equations that model the equilibrium stages are known as MESH Equations:

1. **M**aterial balance equations
2. **E**quilibrium equations
3. **S**ummation equations (mole fractions)
4. **H**eat balance equations

The equilibrium model approach is widely used and gives reliable results for binary and closeboiling, multicomponent mixtures, which can be used in the design of columns and separation processes. However, when the mixtures do not present an ideal or near-ideal VLE behavior, deficiencies in the algorithm start to jeopardize the results. Moreover, the majority of real distillation processes operate away from equilibrium conditions.

An alternative approach has been developed to model distillation and absorption processes, the so-called nonequilibrium (NEQ) or rate-based models. Each stage is not considered anymore in equilibrium, but as an interaction place of two separate phases, that communicate through the mass-transfer phenomena that occur at their interface. Therefore, the mass and energy balance equations gain an additional term, related to the molar flux across the phase interface, as illustrated in Figure 4.2. Recent advances in computational power has allowed more extensive use of this method to solve distillation problems.

The NEQ model requires a flow model to estimate the molar fluxes at the phase interface. This allows for the modeling of additional phenomena in the column, such as bubble or forth formation, at the cost of computational time.

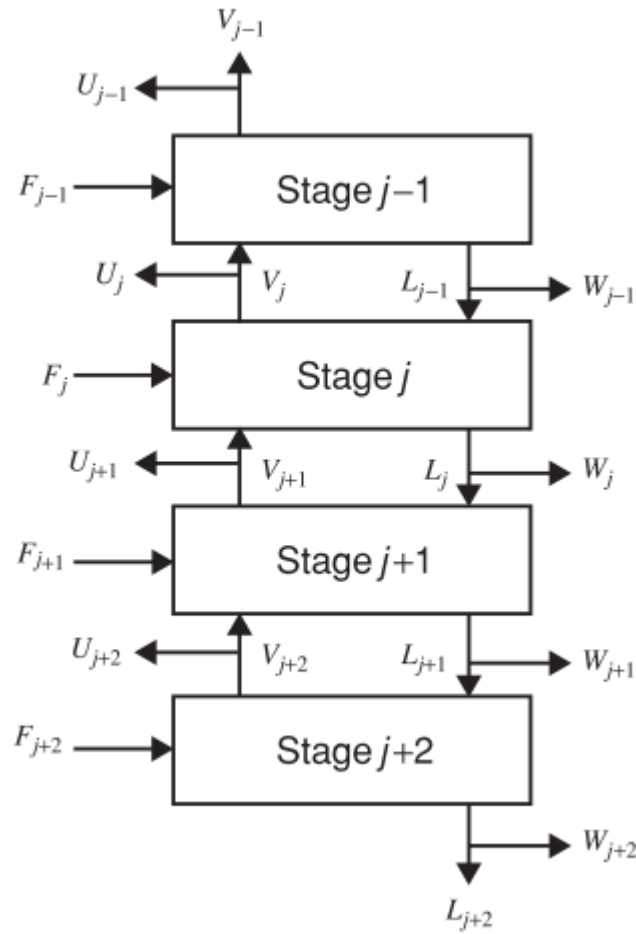


Figure 4.1: Equilibrium-stage model of distillation columns (Green and Perry, 2007).

4.1 Simulation software

To simulate the azeotropic distillation of water-butanol, two different process simulators were used, both currently owned by information technology and engineering consulting company AVEVA™. They are part of the SimSci simulation software package®.

PRO/II process simulator was used for the steady-state simulation and design optimization. It was primarily chosen to ensure compatibility with previous simulations on the other parts of the ABE process, done by Boffa, 2015 and di Pretoro, 2017. Another reason to use PRO/II was the compatibility with the dynamic process simulator DYNsIM, also part of the same

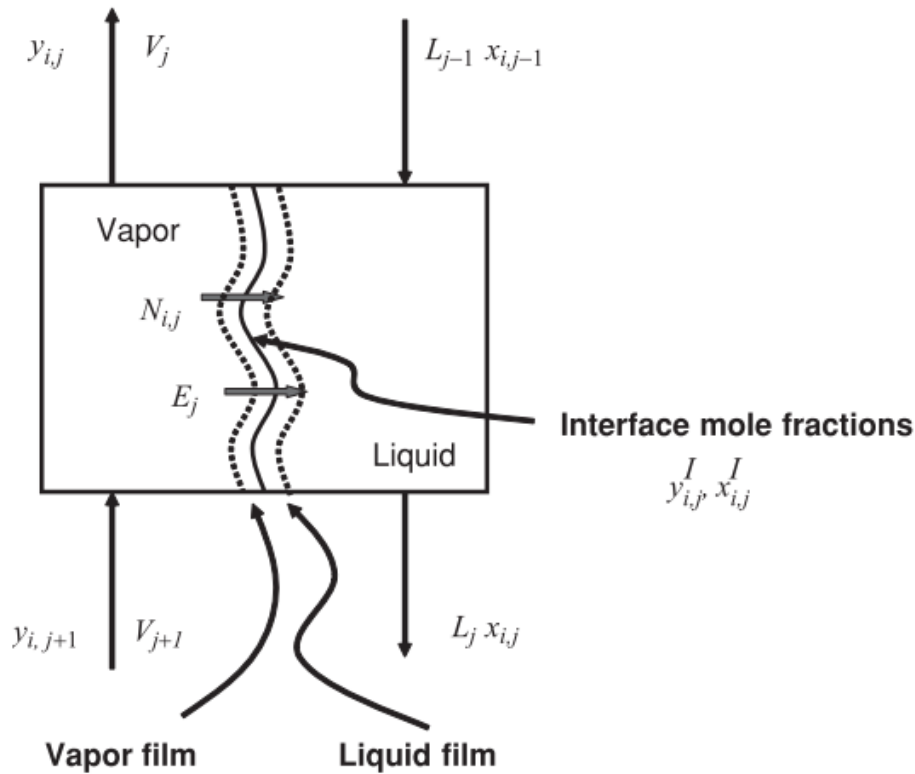


Figure 4.2: A stage of a non-equilibrium model of distillation columns (Green and Perry, 2007).

package, that was used by di Pretoro in the dynamic simulation of the ABE separation plant. However, difficulties appeared when trying to translate the model from one software to the other. Attempts to build the simulation from scratch in DYN-SIM were done, but without success in achieving the steady-state condition to allow further investigations. Reasons are related to the VLLE treatment in the dynamic simulation and the restrictions of models with vapor holdup.

SimCentral™ Simulation Platform was the other simulator used in this work. It was made available on the market in 2017 and it is part of a newer generation of process simulators. Its philosophy is to serve as a complete process platform, allowing for both steady-state and dynamic simulation, and also equipment rating, process optimization and operator training. It is composed of three distinct modes:

- Process Mode: steady state heat and mass balances for design of processes
- Fluid flow mode: steady state used to rate piping and/or equipment design
- Dynamic mode: process dynamics based on equipment design and control system

The user can take advantage of all three modes, applying them for the same PFD and switching on-the-fly. This eliminates the necessity of building different simulations on different software. SimCentral was used to simulate the azeotropic distillation of water-butanol in all three modes.

It is worth to clarify that PRO/II and SimCentral are two simulation solutions based on different computational approach. PRO/II is sequential-modular, as most of the simulation software commercially available, whereas SimCentral is equation-oriented.

In the sequential-modular approach, model solution starts from the feed streams and the process units are solved in sequence, as they appear in the PFD. This means that each equipment has its own set of equations that need to be satisfied locally, despite all other equipment involved in the process. Then all modules are put together and global material flow is checked. If necessary, a new iteration restarts the calculation until convergence has been achieved.

As advantages, it is clearly easy to use and easy to troubleshoot, since every equipment can be investigated separately. On the other hand, it is also clear that recycles present an additional challenge for this method, as they relate the solution of different equipment, leading to convergence difficulties. Other disadvantages include the limited capability of optimization (because the units do not “see” each other) and the creation of custom models.

In the equation-oriented approach, the whole process flow diagram is treated as one set of equations, that needs to be solved simultaneously. This

is particularly useful to solve complex PFDs: there's no need to follow the inlet-to-outlet direction, allowing any degree of freedom of the system to be used for specification. Moreover, recycles are treated simply as an additional equation in the system, reducing issues with convergence and reducing also computational time for large PFDs. The main disadvantages of this method are the high dependency on the initial guess and the big effort necessary to debug the simulation when convergence is not achieved, because it is difficult to isolate the issue.

4.2 Strategies for convergence

Nowadays the methods for solving distillation problems are fairly reliable. Many simulation software allow the user to choose between different computational methods (distillation algorithms) to solve the equations, rendering the solution of distinct distillation problems easier. At the same time, convergence problems are common when simulating distillation, either on sequential-modular approach or in equation-oriented approach. They can be particularly relevant when simulating large PFDs or separation processes that show a high degree of interdependence. Usually, the main causes of convergence issues are wrong specification (unsuited or different from degrees of freedom) and poor initial estimates. Moreover, the convergence difficulty increases with increasing nonideality of the system.

There are a number of strategies users can resort to achieve convergence more easily. Currently, the vast majority of the simulators allow to restart the calculation from a previous iteration or a previous steady-state result. This way, a problem can be solved under a similar, easier to converge condition and then serve as starting guess for the more complex problem; a sort of manual iteration. An example is the simplification of thermodynamic models, for instance adopting Raoult's law instead of using a more complex activity model, such as NRTL or UNIQUAC. The first model can provide an initial, approximate solution of a distillation problem. Although not representing

the real case completely, it is closer to the actual solution of the problem. Another alternative is to reduce the number of interaction parameters of a activity coefficient model. As a general rule, the most strongly nonideal systems are the ones that exhibit two liquid phases (Green and Perry, 2007).

Another common convergence strategy for simulations involving more than one equipment, such as detailed distillation columns, is to add the equipment one at a time, solving the flow sheet at each addition. This approach helps a sequential-modular simulator to solve easily by providing streams completely solved at the inlet of the subsequent equipment. Naturally, recycle loops are the last ones to be closed in this approach, since they affect the whole flow sheet—or process section where it belongs. Moreover, this approach is of particular importance for equation-oriented simulators, because it allows much easier troubleshooting and debugging of the process.

In fact, it is extremely difficult, to say the least, to debug a simulation built with several equipment at a time from scratch. Another reason for this approach is when dynamic simulation is generated directly from the steady-state simulation, as is the case with SimCentral. In this scenario, the equipment's pressures need to be finely tuned in order to allow the start of dynamic mode, otherwise there is no drive for fluid flow (i.e., pressure difference), or strange behaviors may happen, such as reverse flow and controllers failure.

Apart from those general strategies mentioned above, the following ones were adopted for simulation in PRO/II:

- a) Thermodynamic model: simulations were carried out using UNIQUAC model with standard database parameters and NRTL model, both with standard database parameters and custom parameters (as discussed in Chapter 3);
- b) Distillation algorithm: the algorithm ChemDist was used to solve both columns, as opposed to the Inside-Out (software standard). It is a proprietary SimSci method, recommended by the software company to

solve highly non-ideal distillation columns. Generally works best for three-phase distillation simulations;

- c) Column convergence tolerance: water column was the one more difficult to converge. Therefore, initially the tolerance for column convergence was reduced by two orders of magnitude, to 0.01. When first runs converged, tolerance gradually was changed to the standard one;
- d) Valid phases: two liquid phases were considered for all equipment of the process.

For the simulation in SimCentral, the following convergence strategies were adopted:

- a) Thermodynamic model: simulations were carried out using NRTL model with standard database parameters only. Custom parameters revealed inefficient to simulate two liquid phases. The reason is unknown, but may be related to the software's algorithm, as the manual states that VLLE is still under development;
- b) Valid phases: two liquid phases were considered only for the decanter, through the *Fluid Change* block. In practice, two different fluids with same thermodynamic package were declared in SimCentral. For one, only VLE was allowed; for the other, only VLLE. It was identified during the simulations that the column model does not converge with VLLE thermodynamics. Therefore, this maneuver reduces the computational effort on the simulator and allows the columns to achieve convergence. It is worth noting that, with this procedure, it is not possible to prevent the existence of two liquid phases in the columns. In normal operation conditions, i.e. low concentration of butanol, this will not happen, as determined by the thermodynamic of the mixture. However, it is not possible to simulate intermediate situations and their effect in the process as a whole.

In general lines, the following method was used to achieve convergence of the process in both simulators:

1. Simulate simplified water column: initially, a simplified model containing a partial condenser and reboiler is used to simulate the water column. It allows to obtain a first guess of the duty on the reboiler and the reflux flow rate;
2. Reflux dummy stream: once first guess is obtained, condenser is removed from the model and a dummy stream identical to the reflux one is added to the reflux inlet. This eliminates the necessity of the condenser to solve the column;
3. Detailed water column reboiler: if the case, the reboiler can be now externalized for detailed simulation of steam stream and sizing;
4. Condenser and decanter: top stream of first column is then connected to a simplified condenser, specified to zero vapor fraction at the outlet, allowing to obtain condenser duty. Then, outlet stream is connected to a three-phase decanter, where phase separation occurs;
5. Simulate simplified butanol column: as for the first column, butanol column can now be simulated starting from a simplified model, having as feed the organic phase from the decanter. However, it is not necessary to simulate the internal condenser, as this column can be seen as a simple stripping column;
6. Detailed butanol column reboiler: same as point 2;
7. Close loop on butanol column: now the overhead of butanol column is connected to the condenser (via a mixing block), closing the loop of the organic side;
8. Close loop on water column: at last, reflux dummy stream is removed to close the loop on the water column.

4.3 Process Flow Diagrams

Figure 4.3 shows the PFD of the process conceived in PRO/II for a feed stream containing up to 10% mol of butanol, whereas Figure 4.4 shows the PFD for feed containing above this percentage.

Figure 4.5 shows the PFD of the steady-state solution carried out in SimCentral for feed up to 10% mol butanol, while Figure 4.6 shows the PFD for concentrations over 10%.

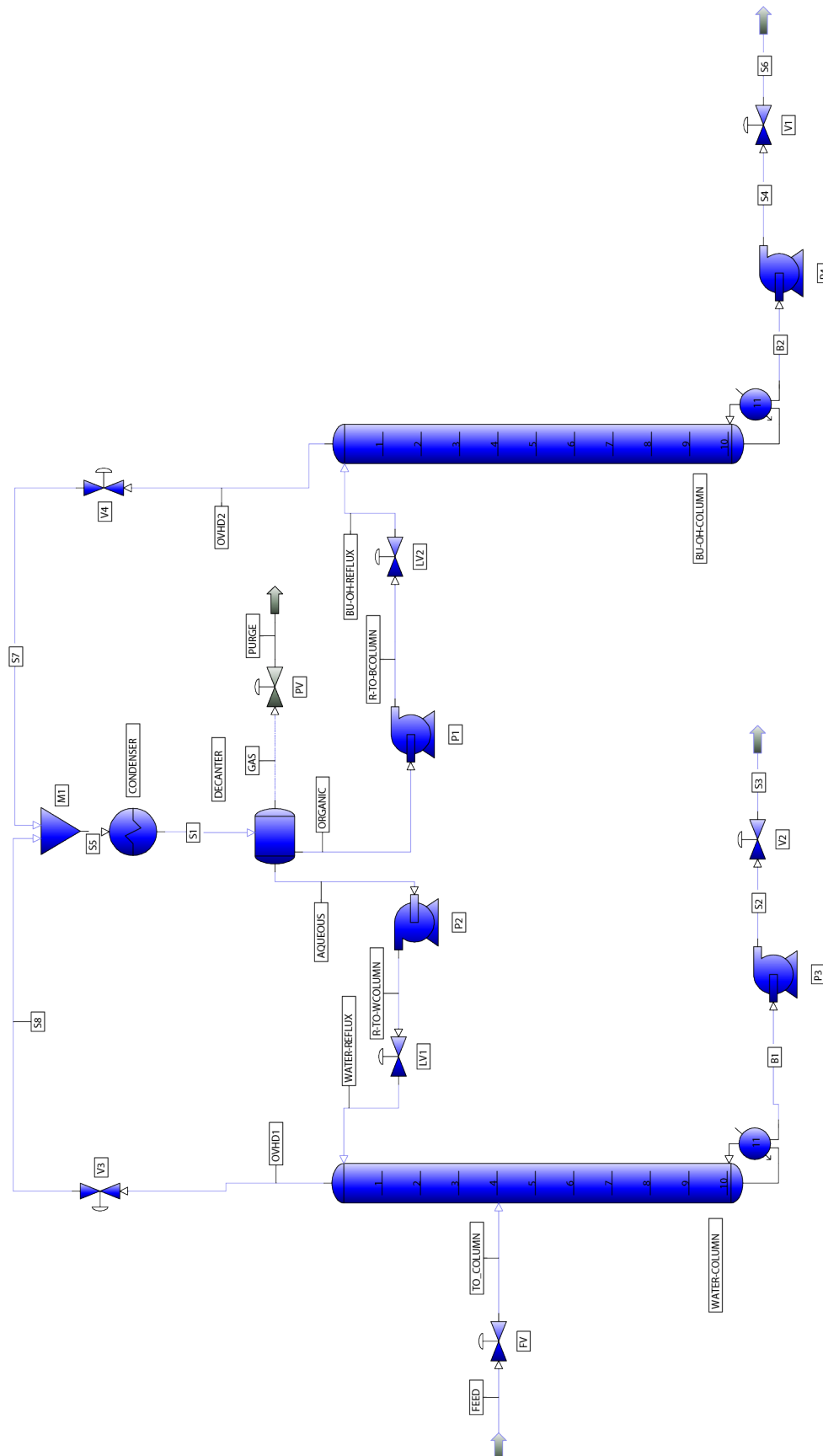


Figure 4.3: Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} < 0.1$ in PRO/II.

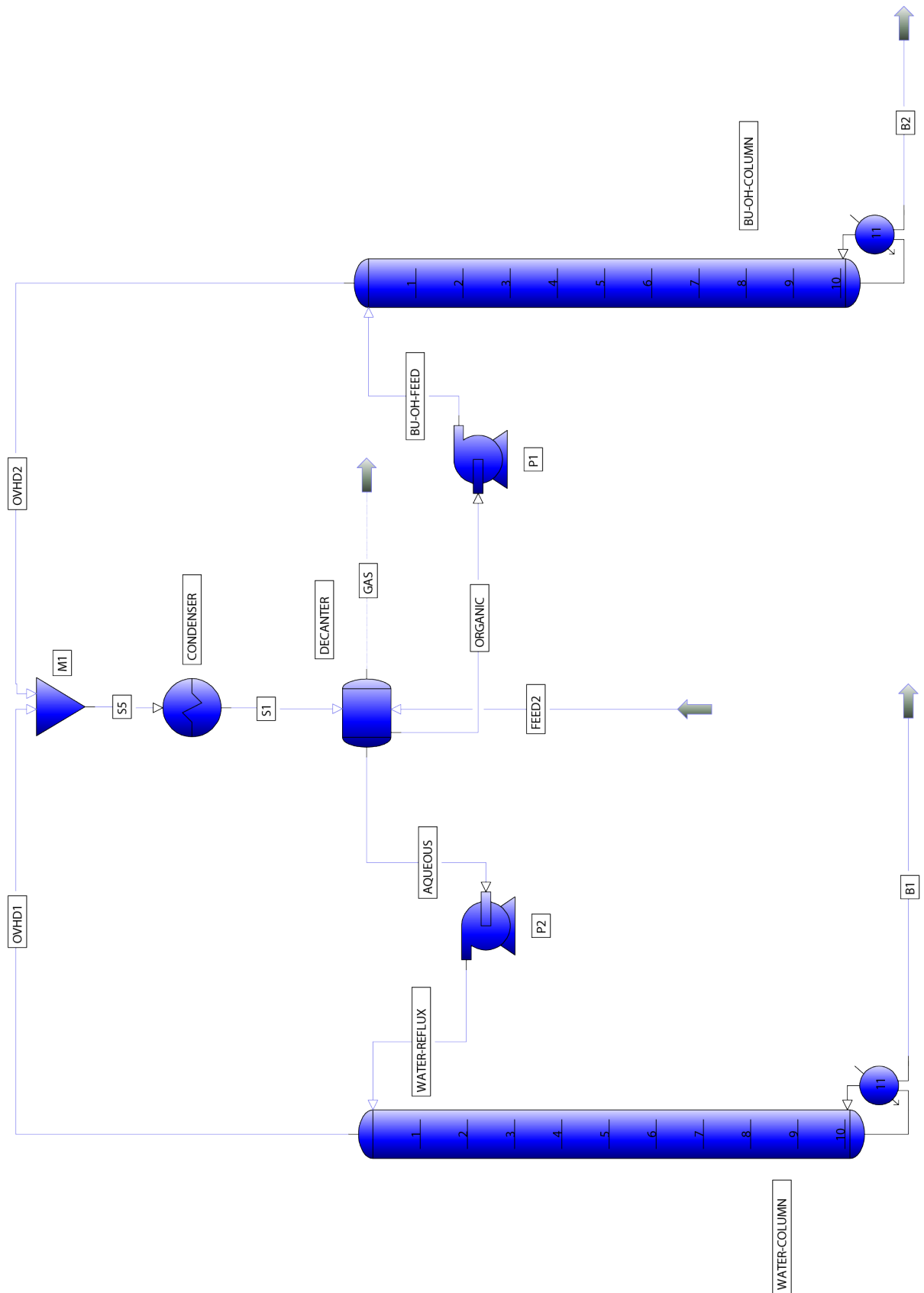


Figure 4.4: Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} > 0.1$ in PRO/II.

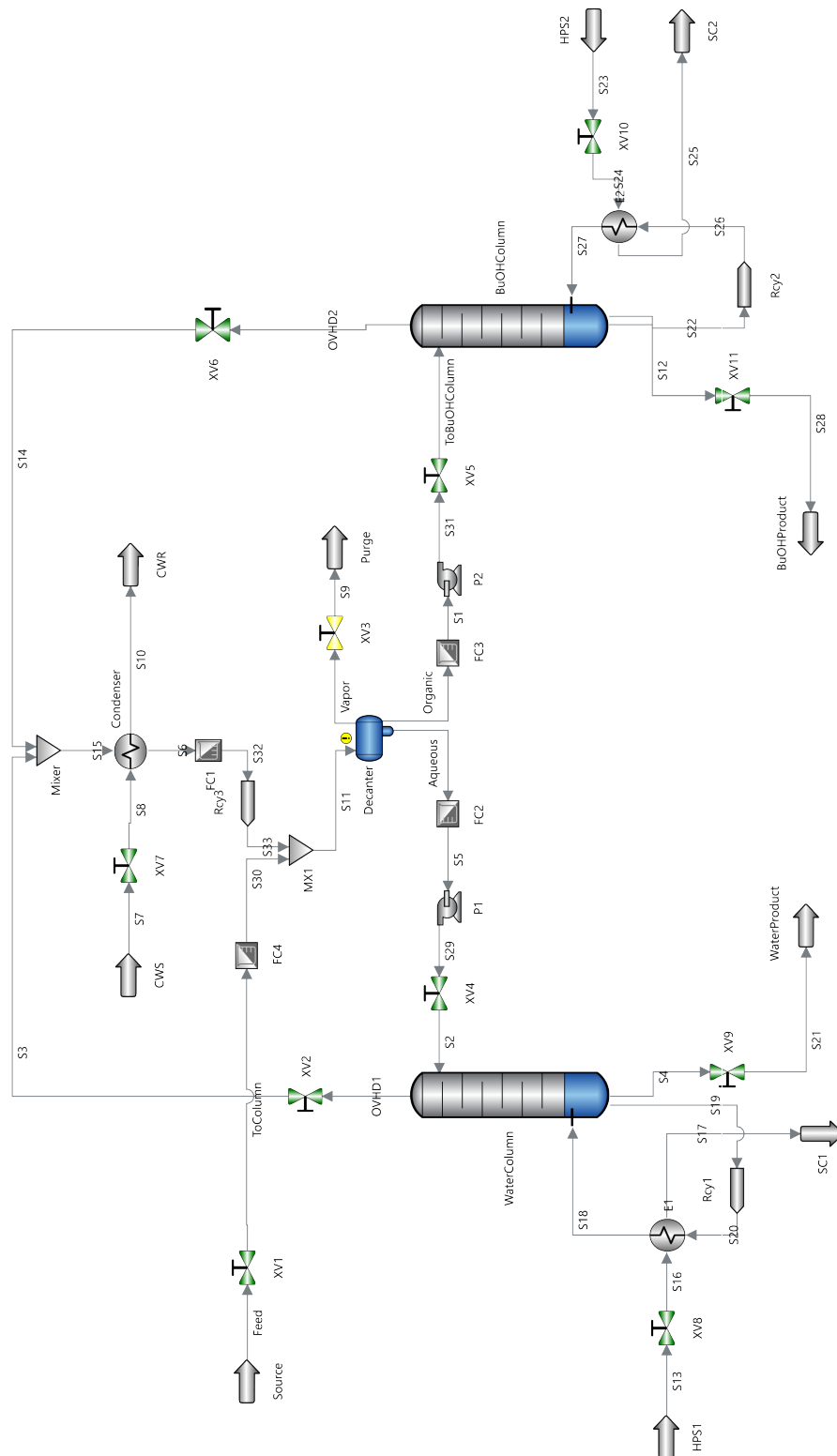


Figure 4.6: Concept engineering PFD of water butanol separation process for feed with $z_{BuOH} > 0.1$ in SimCentral.

4.4 Steady-state results

4.4.1 The base case

The conditions of feed stream, valid for all simulations, and of the base case for the separation of water and butanol are resumed in Tables 4.1 and 4.2, respectively. It takes into account the nominal composition of the water-butanol stream from the separation train and the consideration that both columns can have the same number of trays, as observed in the previous studies of the SuPER Group. One can also arrive at the same last conclusion by observing the T-x-y diagrams of Figures 3.2 and 3.3 and noticing that each column will work on opposite sides of the azeotrope composition, since the azeotrope will be broken by phase separation in the decanter. Therefore, as the curve is quite similar for both sides, it is reasonable to consider that both columns will have similar number of stages.

Table 4.1: Standard feed conditions for separation of water and butanol

Flow rate	kmol/h	1000
Temperature	K	350
Pressure	atm	0.5
Phase	-	liquid
Stream composition		
Water	%mol	0.96
n-Butanol	%mol	0.04

Table 4.2: Conditions and specifications for base case simulation

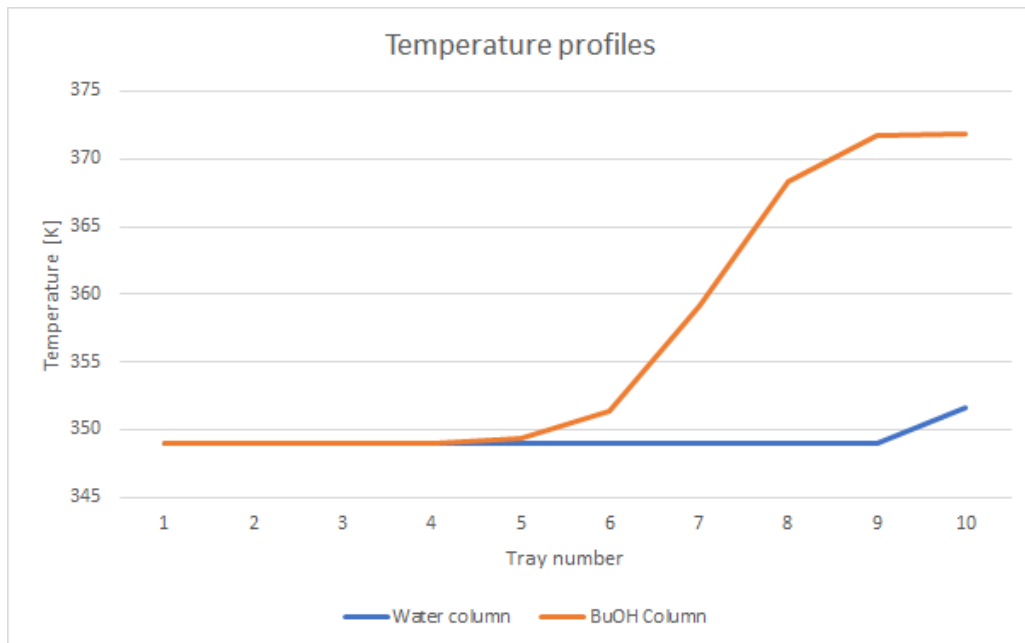
Water column pressure	atm	0.5
Butanol column pressure	atm	0.5
Water purity at bottom of water column	%mol	0.999
Butanol purity at bottom of butanol column	%mol	0.999
Cooling water temperature	°C	25

The main results of the base case as simulated in PRO/II with the process depicted in Figure 4.3 are summarized in Table 4.3. For 10 tray columns operating at pressure of 0.5 atm, the energy requirement in the reboilers are

Table 4.3: Steady-state results for main streams in the base case

Stream	FEED	B1	B2	REFLUX BCOLUMN	OVHD1	OVHD2	REFLUX WCOLUMN
Phase	Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Liquid
Temperature [K]	347,5	354,1	372,5	343,9	349	349	343,9
Pressure [atm]	0,5	0,5	0,5	0,5	0,5	0,5	0,5
Flow rate [kmol/h]	1000	960,92	39,08	146,55	187,95	107,47	148,87
Molar Composition							
Water	0,96	0,999	0,001	0,5759	0,7856	0,785	0,9915
Butanol	0,04	0,001	0,999	0,4241	0,2144	0,215	0,0085

$Q_{R1} = 2.3628MW$ and $Q_{R2} = 1.3743MW$, while the duty in the condenser is $Q_{Cond} = 3.5900MW$ (R_i stands for the reboiler of column i). The butanol recovery with respect to the feed is of 97.69%.

**Figure 4.7:** Temperature profile of water column and butanol column for base case

The temperature profiles of the columns for the base case are shown in Figure 4.7. It can be observed that the water column has an almost flat profile, increasing the temperature only at the last stage and the reboiler. It

is coherent because the feed and the reflux from the decanter are very rich in water, so there is no need for big changes in temperature. The butanol column, in its turn, shows a considerable increase in temperature from the 5-th stage to the reboiler, which is also coherent considering the boiling point of butanol (117 °C).

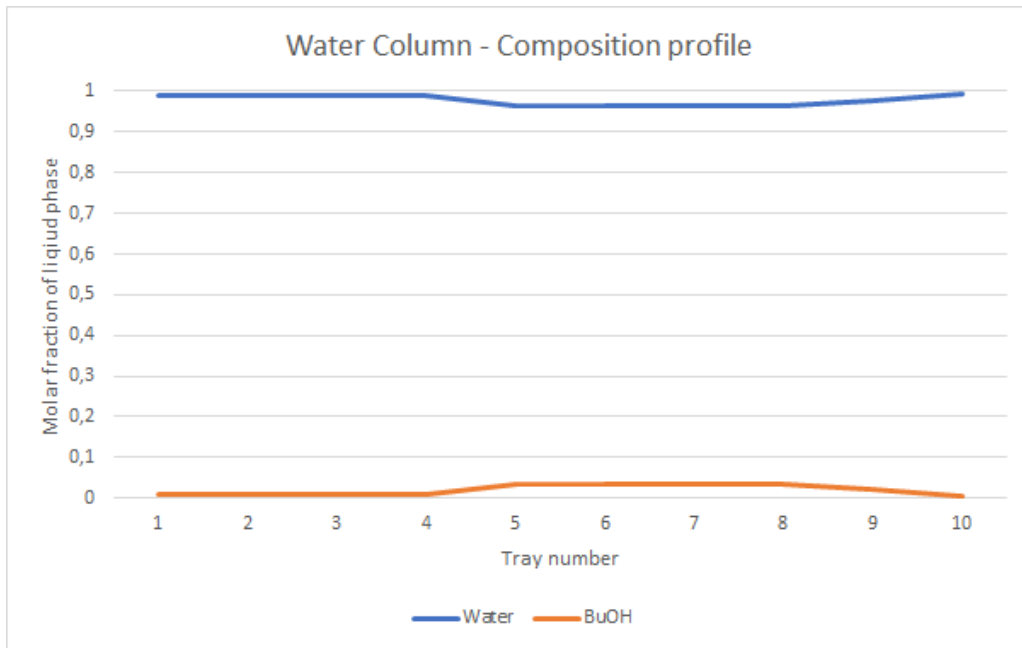


Figure 4.8: Composition profiles of liquid phase for the water column in the base case

The molar composition profiles for the base case are shown in Figures 4.8 and 4.9. Again, as the water amount is much higher, water column shows an almost flat profile, while butanol column presents a flat profile until 6-th tray, when butanol fraction increases to the desired specification of 99.9%.

The liquid and vapor rate profiles are shown in Figure 4.10 for water column and Figure 4.11 for butanol column. For the first, vapor increases throughout the whole column, while liquid shifts from a lower, constant value a higher one after stage 5. For the second, both phases show the same flow profile. Proportionally, the butanol column has much more vapor in it, which is in line with the fact that it behaves as a stripping section, which demands higher vapor flow rate for separation. Still, vapor flow rate of water column is higher in absolute numbers, and as it is directly related to the diameter of the

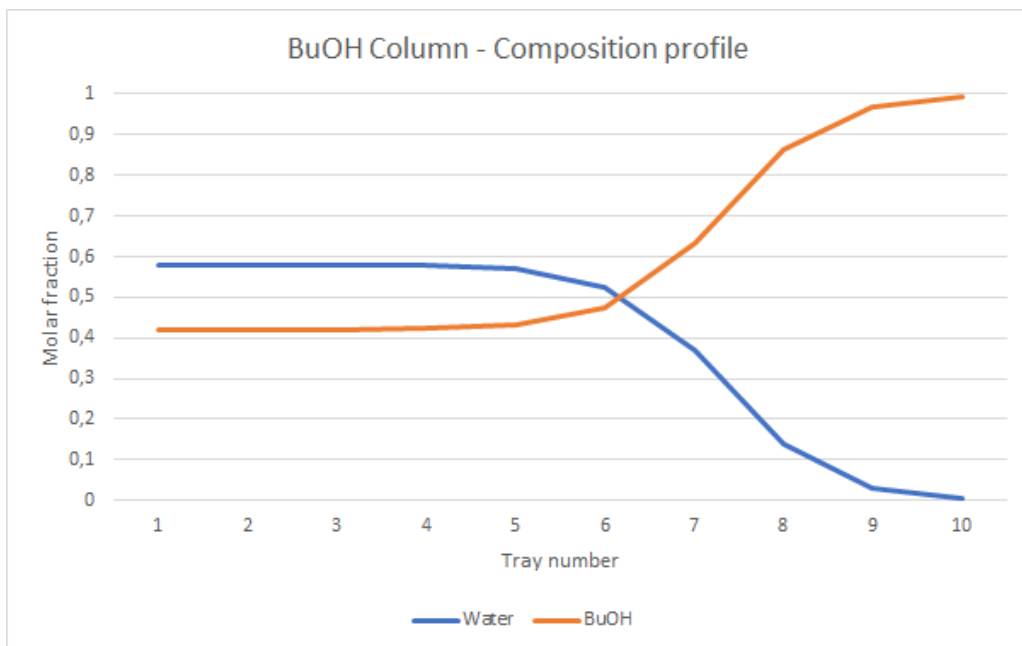


Figure 4.9: Composition profiles of liquid phase for the butanol column in the base case

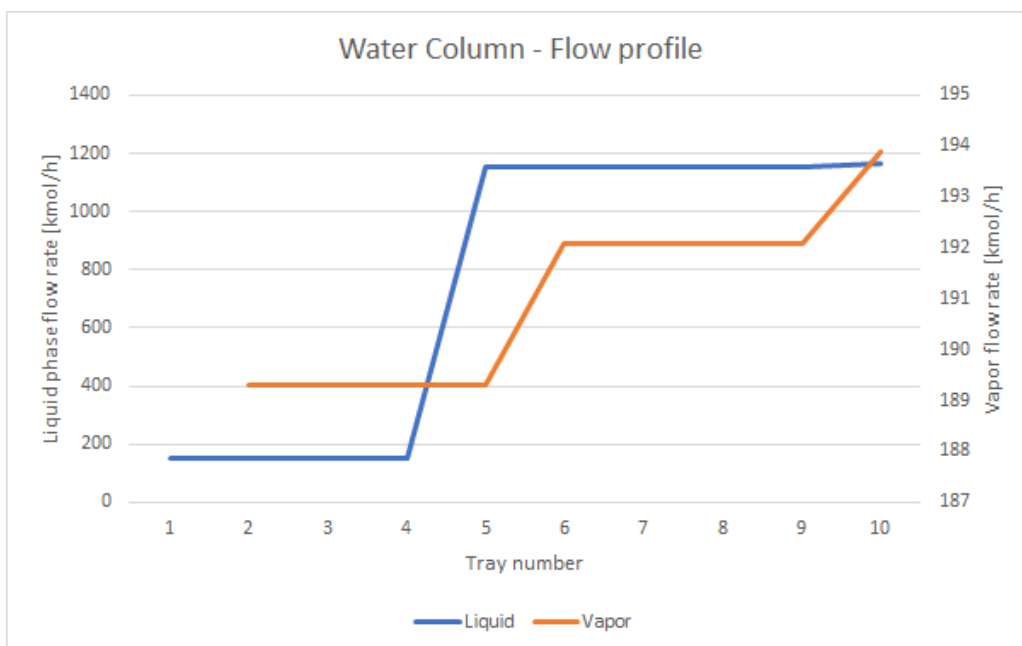


Figure 4.10: Flow profiles of liquid and vapor phases for the water column in the base case

column, it is possible to affirm that the water column will have larger capital expenditure (CAPEX) when compared to the butanol column in the base case, considering that they have the same number of trays. This situation will invert as the fraction of butanol grows higher, as will be discussed in

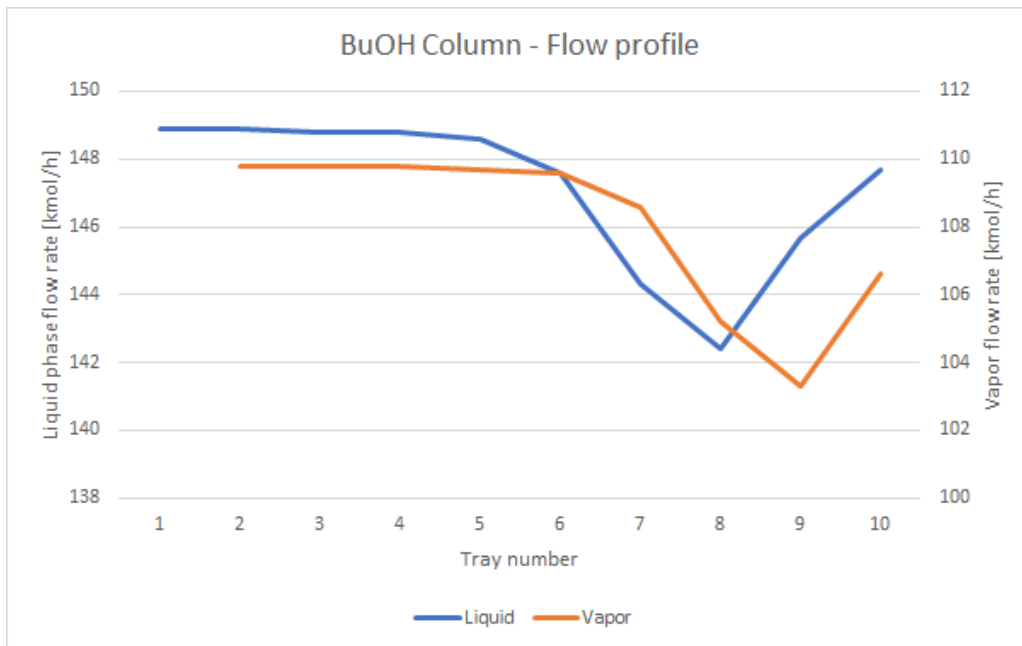


Figure 4.11: Flow profiles of liquid and vapor phases for the butanol column in the base case section 4.4.3.

In addition to the base case with 4% molar, a case with 40% molar of butanol based on the PFD of Figure 4.4 was run. As expected, the higher amount of butanol in the feed shifted the energy requirement to the second column of the scheme; detailed analysis of this will follow, in section 4.4.3. The profiles, however, have qualitatively the same shape and are, therefore, not presented. This result confirms, however, that the process conceived is robust enough to deal with a broad range of butanol fractions, which is an important result considering that this is the last part of the separation in a ABE Plant. If previous parts of the process are debottlenecked and the feed get enriched in butanol, the proposed process is up to the challenge, from mass and energy balance point of view.

4.4.2 Condenser and reboiler evaluation

To evaluate the influence and importance of the thermodynamic model to the simulation, an analysis of the energy demand of the heat exchangers for

different methods was carried out. Since in the base case the two columns are equal, by changing the model, one can verify the effect in the duty required for the new equilibrium conditions. This is important because it has a direct relation to the cost of the heat exchanger, as the surface area of the equipment is proportional to the duty. It affects other parameters of the process, such as the column sizing due to the changes in internal flow. However, for the purpose of comparison, only the heat exchangers were considered.

For this analysis the following thermodynamic packages in PRO/II were considered:

1. NRTL Standard: PRO/II database parameters;
2. NRTL Adjusted: custom parameters (see Table 3.2)
3. UNIQUAC: PRO/II database parameters.

Calculations were carried out for feeds containing 2%, 10% and 40% mol butanol. As verification, the results were compared to the ones obtained by Luyben, [2008a](#), that simulated the same process using UNIQUAC thermodynamic model and the simulator Aspen Plus, by AspenTech. Results are shown in Figures 4.12 to 4.14.

From the figures it can be observed that there is a tendency in the duties, as the differences among the models for the same equipment tend to be similar when butanol concentration is changed. An increase in the duty of butanol column is noted when the concentration of this component is increased, which is also expected, because the effort of the separation shifts from the first column to the second column.

The model NRTL Adjusted tends to underestimate the duty compared to the other models, except for low concentrations of butanol. This is probably related to the experimental data used to regress the parameters. Nevertheless, it is much more aligned with standard database parameters when compared to the results obtained by Luyben. In fact, reboiler duty of water column for

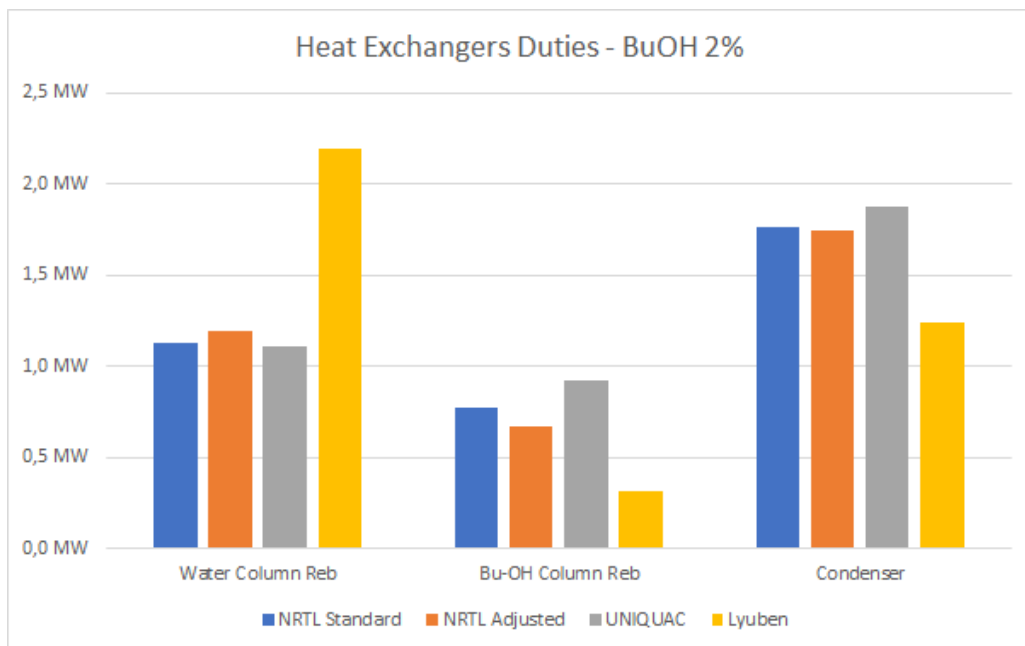


Figure 4.12: Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 2\%$ for different thermodynamic models

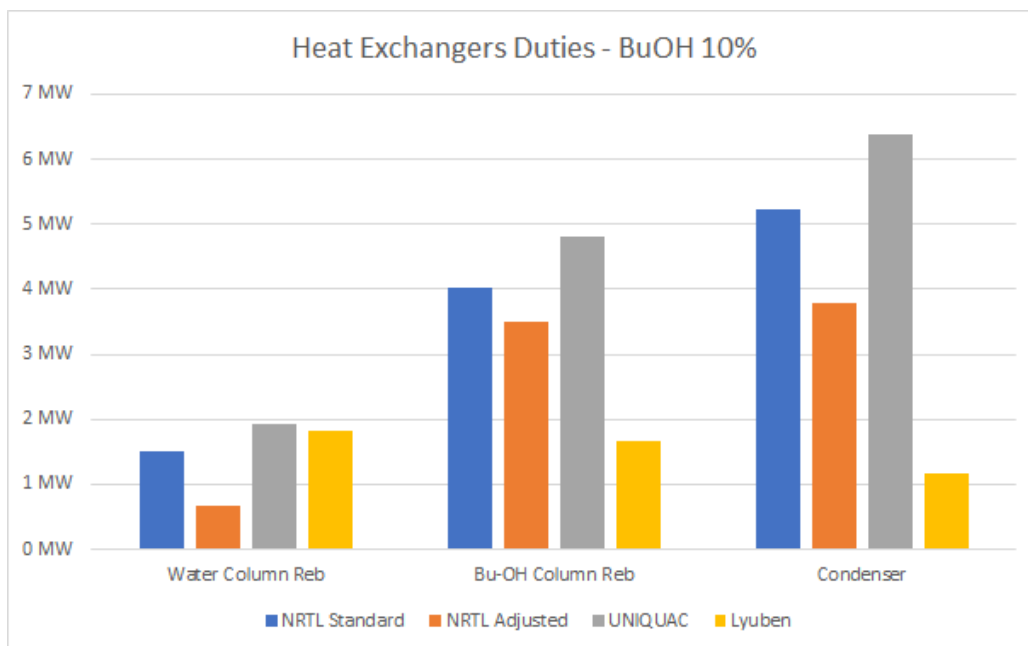


Figure 4.13: Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 10\%$ for different thermodynamic models

2% BuOH content from Lyuben is much higher than the other simulations. Moreover, the condenser duty in his results appears to have a decreasing

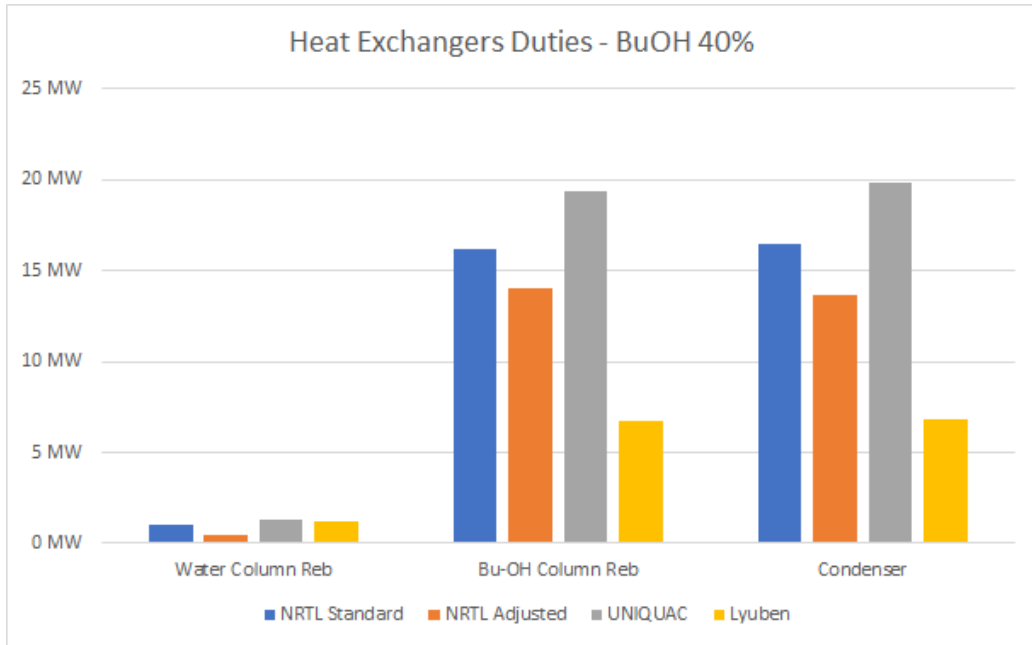


Figure 4.14: Comparison of reboilers and condenser duties for feed with $z_{BuOH} = 40\%$ for different thermodynamic models

trend with the increase in butanol fraction.

This last observation is not in line with the general behavior of the process. In fact, when butanol fraction is increased, the stream condition is shifted to the opposite side of the azeotrope composition, as already discussed in section 4.4.1. This causes a higher flow from top of butanol column into the condenser, because more vapor flow is needed to achieve the same separation. Therefore, it is expected that the condenser duty is higher for higher butanol fractions. Moreover, duty should be linear with the flow, as states the energy balance equation for a stream in a heat exchanger (4.4.1), considering that the C_p is very similar. Figure 4.15 illustrates this reasoning by plotting the duty in the condenser as function of the inlet flow rate, showing that the results published by Luyben are not aligned with the physics of the process.

$$Q = \dot{m}C_p\Delta T \quad (4.4.1)$$

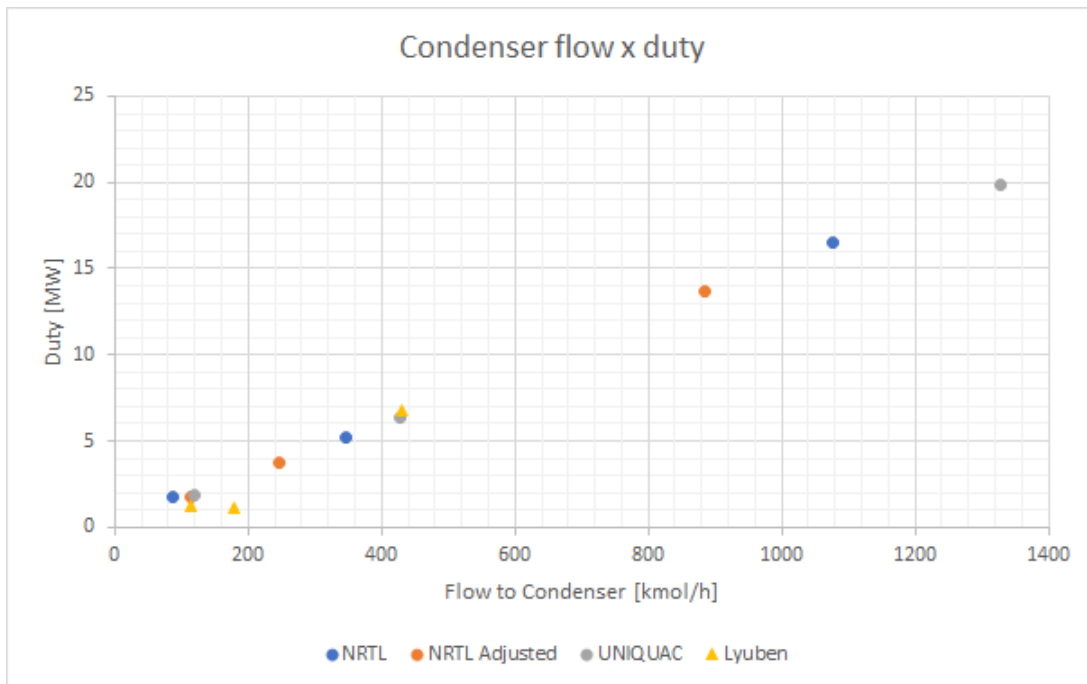


Figure 4.15: Flow rate to condenser versus condenser duty for different butanol fractions

4.4.3 Sensitivity analysis and design optimization

The base case assessed the feasibility of the process and the associated energy consumption. For the optimization of the design, a number of variables can be taken into consideration, and different methods are possible. A rather simple approach is to run a sensitivity analysis in the simulator to verify the impact of a variable in the overall results; most simulators already have this tool embedded. The Case Study feature of the simulator PRO/II was used to generate two different scenarios for design optimization.

The main design variables that impact CAPEX in this process are: columns' diameter and heat exchangers' areas. The former depends on the column internal flows, particularly the vapor flow rate, while the latter depends on the duty necessary for separation. In section 4.4.1 the internal flows for the base case were discussed, reporting that vapor flow is much higher in butanol column compared to the water column. It was shown in section 4.4.2 that the condenser duty is function of its inlet flow, that in turn depends on the fraction of butanol. Both are directly proportional to the performance of the

separation. Therefore, the variables chosen for a sensitivity analysis were the number of trays and the pressure of each column.

For the first analysis, the number of trays in one column was varied from 5 to 20, in intervals of 5 trays, while the other column was kept constant at 10 trays; same process was repeated for the other column. Two feed conditions were considered, namely: 4% butanol fraction (using PFD from Figure 4.3) and 40% butanol fraction (using PFD from Figure 4.4), making a total of 14 different case scenarios. For each one of them the duty of the heat exchangers is compared, along with the total energy consumption for the separation. Conditions for each case and the respective results are shown in Table 4.4.

Table 4.4: Sensitivity analysis for the number of trays in each column

Case	BuOH molar fraction [%]	# Trays		Reboiler Duty [MW]		Condenser Duty [MW]	Total Energy Consumption [MW]
		Water Column	BuOH Column	Water Column	BuOH Column		
1	4	5	10	3,3499	1,3774	4,5782	9,3055
2	4	10	10	2,3628	1,3743	3,5900	7,3271
3	4	15	10	2,3628	1,3743	3,5900	7,3271
4	4	20	10	2,3628	1,3743	3,5900	7,3271
5	4	10	5	2,3628	1,4399	3,6555	7,4582
6	4	10	15	2,3629	1,3747	3,5900	7,3276
7	4	10	20	2,3629	1,3745	3,5900	7,3274
8	40	5	10	0,4495	14,0591	13,6797	28,1883
9	40	10	10	0,4397	14,0658	13,6760	28,1815
10	40	15	10	0,4386	14,0564	13,6662	28,1612
11	40	20	10	0,4389	14,0605	13,6703	28,1697
12	40	10	5	0,4391	14,7372	14,3483	29,5246
13	40	10	15	0,4391	14,0576	13,6678	28,1645
14	40	10	20	0,4391	14,0508	13,6682	28,1581

For low butanol fraction, the results indicate that the design with 10 trays for each column is the most efficient one in terms of energy consumption (case 2 in Table 4.4). For high butanol fraction, the most efficient design is the one with 10 trays for water column and 20 trays for butanol column (case

14 in Table 4.4).

When water column is the smallest, the reboiler duty is the highest one, no matter the concentration of butanol. Moreover, there is a negligible difference in the reboiler duty for this column when the number of trays is bigger than 10, mainly because the reflux ratio is practically constant in this situation. As the number of trays increases, for constant butanol column, the duty in the reboiler reaches a plateau, indicating that it is not effective, from separation point of view, to make the water column too high.

This is coherent with the fact that separation in the water column is relatively easy, given that it will always be the most concentrated species in the feed. However, there is an important increase in the reboiler and the condenser duties when water column has less than 10 trays and the concentration of butanol is small. Case 1 has reboiler duty 40% higher, and condenser duty 27% higher, than other cases. When butanol fraction is higher, this difference drops to 2% in the reboiler and 0% for the condenser.

For butanol column, reboiler duty is reasonably constant, except when the number of trays is smaller than 10. Nevertheless, the difference between case 1 (number of trays = 5) and the others is less than 1%, in a way that it can be said there is no appreciable difference between the scenarios for the butanol column. This means that it is possible to choose the column with low number of trays, which influences directly the CAPEX of the equipment. As expected, reboiler duty for this column in the high BuOH fraction scenario is much higher than the previous one. This is because there is much more butanol to be separated, and there is a substantial difference in the boiling point of both species, as explained in section 4.4.1.

As for the condenser duty, excluding the higher value for $z_{BuOH} = 0.04$ and water column with 5 trays, there is no difference between the cases for same butanol fraction. Moreover, it tends to reduce as the butanol fraction is higher, because the job is transferred to the reboiler of the butanol column, as explained in the previous paragraph. Therefore, it is possible to conclude that

the condenser duty is inversely proportional to the butanol fraction in the feed. However, as discussed in section 4.4.2, flow to the condenser increases with butanol fraction. The net result in the CAPEX for this equipment must be assessed considering this information and affects directly the decanter sizing as well. Figure 4.16 shows graphically the results of the sensitivity analysis of the number of trays, clearly identifying the shifts and trends in the energy consumption.

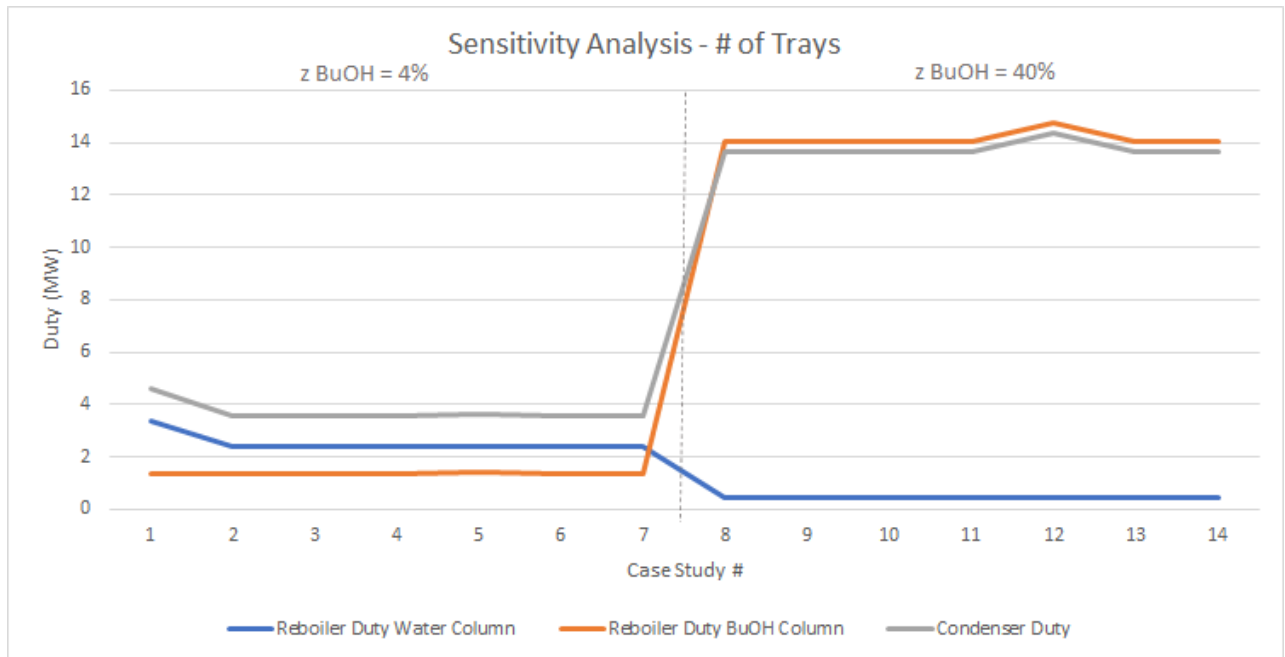


Figure 4.16: Energy consumption for sensitivity analysis of the number of trays. Cases 1 to 7 are for $z_{BuOH} = 4\%$; cases 8 to 14 are for $z_{BuOH} = 40\%$

For the second analysis, the energy demand of the process was compared for columns pressures of 0.5 atm and 1 atm, for three different butanol fractions in the feed, namely 2%, 10% and 40%. The thermodynamic parameters used here are the custom ones, which were adjusted to the pressure of 1 atm. However, it is known that pressure has little to negligible influence over this parameters, especially for small values (Prausnitz *et al.*, 2000). Therefore, the same parameters were used for both pressures. Moreover, for this same reason and because the azeotrope is heterogeneous, there is no reason to test a scenario where each column operates at a different pressure. Same reasoning applies for scenarios with pressure above the atmospheric one,

which would also add the disadvantage of increasing the boiling point of the species and, consequently, the energy consumption. Conditions for each case and the respective results are shown in Table 4.5.

Table 4.5: Sensitivity analysis for the pressure of both columns

Case	Butanol molar fraction [%]	Pressure [atm]	Reboiler Duty [MW]		Condenser Duty [MW]	Condenser Temp. [K]	Total Energy Consumption [MW]
			Water Column	BuOH Column			
1	2	0.50	1,1928	0,6697	1,7491	343	3,6116
2	10	0.50	0,658	3,491	3,7848	343	7,9338
3	40	0.50	0,4391	14,0576	13,6678	343	28,1645
4	2	1	1,131	0,8144	1,8184	363	3,7638
5	10	1	0,8241	4,0424	4,0086	363	8,8751
6	40	1	0,5501	16,2738	14,8933	363	31,7172

It can be observed that the total energy consumption for same butanol fraction at different pressures is very similar, in terms of absolute number. However, looking closer at the percentage difference, it spans from -4% to -11% energy consumption of case with $P = 0.5atm$ with respect to the other, for same BuOH fraction. Therefore, it is not negligible and the operation at lower pressure is a better choice. At this pressure, temperature at the condenser —and consequently, at the decanter —is still high enough to allow the use of cooling tower water, usually with temperatures that range 10 to 40 °C. Even at its highest, in summer, for example, the driving force for heat exchange would still be of about $\Delta T = 30$ °C, which is more than sufficient for design and operation. Another reason to choose lower pressure is because this process is the last in the series of separation for an ABE Plant. If no high pressure is required, less energy needs to be spend in the initial portion of the separation train.

4.4.4 Comparison of results from both simulators

With the results above from simulations in PRO/II, it was decided to take advantage of SimCentral's integrated approach of process and fluid-flow/dynamic simulation to build the more detailed PFDs in this simulator. Therefore, in the Process Mode, the reboilers of the columns were made explicit, allowing their modeling and the determination of the demanded hot utility, as can be noticed in Figures 4.5 and 4.6. It was also necessary to add the following: pressure elements (valves and pumps), that are required for the other modes, as will be detailed in Chapter 5; dimensions of the decanter, that are not taken into account in PRO/II (only flash calculations are done). The decanter is of type horizontal, with boot for second liquid phase separation. The additional input data is summarized in Table 4.6.

Table 4.6: Additional specifications for simulation in SimCentral - Process Mode

Steam supply pressure	bar	4.75
Steam supply temperature	°C	150
Vapor fraction of steam outlet from reboiler	%	0
Decanter diameter	m	1
Decanter length	m	2
Decanter boot diameter	m	0.5
Decanter boot length	m	0.5

To compare the results from both simulators, the same base case of section 4.4.1 was run using the PDF of Figure 4.5. However, it was not possible to work using custom NRTL parameters and pressures below 1 atm in SimCentral. Probably both limitations are related to the correct calculation of vapor-liquid-liquid equilibrium (VLLE) and liquid phases, as could be identified by the errors in the equations. Therefore, to ensure comparability of results, base case in PRO/II was run again, for pressure equal to 1 atm. The results in terms of energy requirement and butanol recovery are presented in Table 4.7.

It can be seen that duty required for water column and butanol column are similar for both simulators, while the results for the condenser differ

Table 4.7: Compared results of base case with $P = 1$ atm for PRO/II and SimCentral

Variable	Unit	PRO/II	SimCentral
Q_{R1}	MW	1,6698	1,8145
Q_{R2}	MW	2,2813	2,3781
Q_C	MW	3,7269	4,1531
Total Duty	MW	7,6780	8,3457
Butanol Recovery	-	97,64%	97,60%

the most. In general, SimCentral overestimated the duties compared to PRO/II. For the water column, SimCentral's duty is 9% higher, while for the butanol column the difference is of +4%. For the condenser, duty is 11% higher. In the end, total energy requirement is 9% higher for SimCentral with respect to PRO/II. From mass balance point of view though, both simulators achieve the same butanol recovery – hence, the process specification. This is expected as both simulations are flow-driven: global stream energy and mass balance may be satisfied, but intermediate results do not necessarily match the physical phenomena.

This rather important difference in the duties is probably related to thermodynamic data and VLLE. In fact, the version of SimCentral that was used in the present work (4.1.0.1406) does not support completely VLLE calculations. The software's manual cites that it cannot be used in high pressure systems, as well as in fluid-flow and dynamic modes, although for some systems it may work; column models may use fluids with VLLE declared, but errors may occur. To this is added the different thermodynamic parameters for the NRTL model. However, results should be more similar, as encountered during the duty investigation presented in section 4.4.2.

One factor that impacts these results is certainly the thermodynamic parameters. As mentioned, SimCentral did not manage to calculate VLLE with the custom NRTL parameters, and this is most certainly a source of the differences. Another source is related to the simulation itself. As explained in section 4.2, the block *Fluid Change* was used to change the thermodynamics from VLE only to VLLE in models where two liquid phases were present

for sure, namely the condenser and the decanter. It is coherent with the thermodynamics of the mixture, while allowing to escape the simulator limitations in dealing with VLLE. However, this maneuver may have affected other equations of the system, leading to differences in the results between the two simulators.

Despite the discrepancies in the duties, the columns profiles are very similar. The profiles of the process from PRO/II at $P = 1$ atm is the same as the ones showed in Figures 4.7 and 4.11. The ones obtained in SimCentral are virtually the same, as exemplified in Figure 4.17, that shows the temperature and liquid and vapor flow rates profiles for the butanol column. Temperature profile is just slightly different when compared to Figure 4.7, disregarding the difference in the maximum temperature, that is due to the higher pressure of the process. Liquid and vapor flow rates profiles are also very similar, with some minor differences in the first tray.

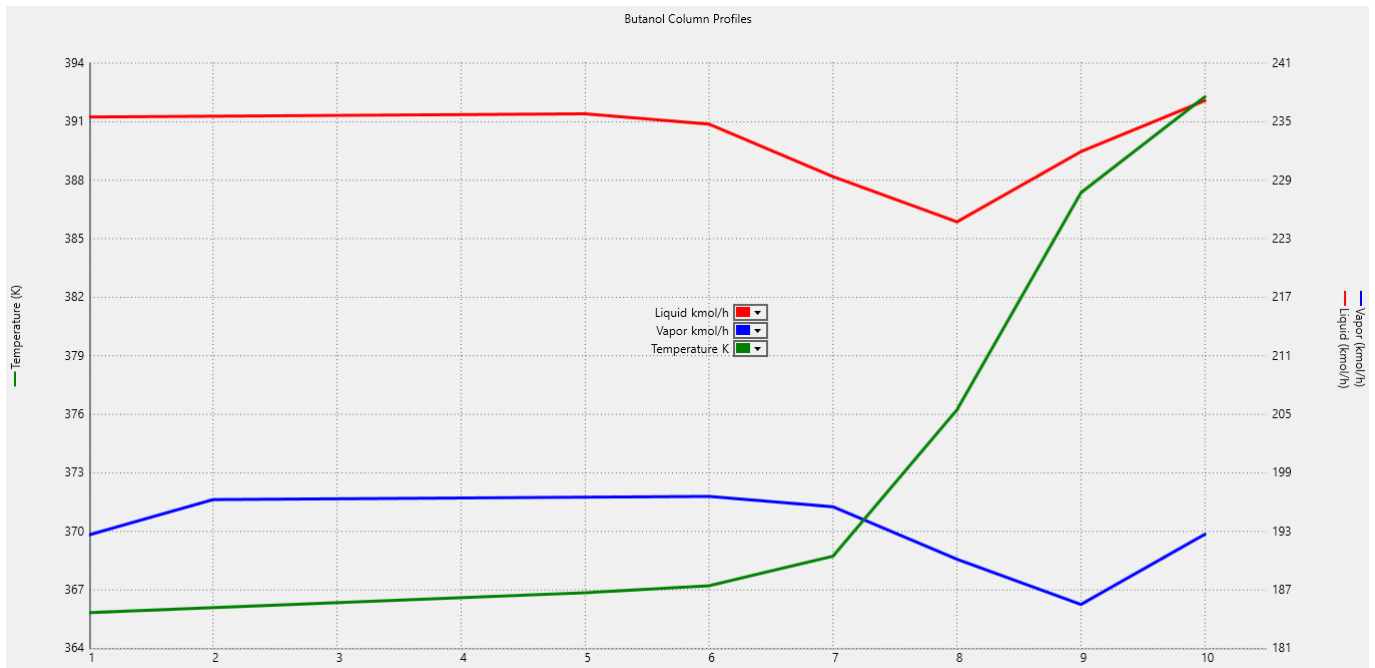


Figure 4.17: Temperature and flow rates profiles for the butanol column in the base case with $P = 1$ atm, as obtained in SimCentral

Considering these results satisfactory, a detailed engineering PFD was developed in SimCentral and the investigations on dynamic simulation will

be briefly discussed in Chapter 5.

Chapter 5

Process Dynamics

5.1 Pressure-driven simulations

Dynamic simulation is a powerful tool to evaluate the response in time of a determined process. It is useful to study the transient behavior (derivative terms) of the process and the effect of disturbances on it, including particular cases such as start-up, shut-down and emergency response of units. It is also useful for the equipment sizing, allowing the optimization based on real-time response of operation conditions, and to development and rating of control strategies, including predictive control.

From a computational point of view, the dynamic simulation is a rather intensive process. It depends highly on mathematical algorithms and problem simplification capacity to deliver reliable results, in a reasonable time. The fast advances in computer science has allowed for the use of dynamic simulators in smaller computers and portable units, collaborating to its spread as engineering tool.

From a simulation point of view, the dynamic simulation can be of two types. The first one, less common, is the *flow-driven* simulation. It works in a similar fashion as the steady-state simulation, where stream flow verification is used to satisfy the balance equations. The second type is the *pressure-driven*

simulation, where the differences in pressure of the system are responsible for the flow, via the momentum balance. Some commercial simulators are able to perform both types of dynamic simulation.

The pressure-driven approach is preferred because it gives a more realistic representation of the dynamics of the process. Consequently, it allows for a more rigorous evaluation of the control scheme and its robustness. Therefore, it is of paramount importance for a pressure-driven, dynamic simulation the realistic (but not necessarily precise) definition of pressures and pressure drops, as well as control strategies and controller tuning.

Taking advantage of the features of SimCentral, the PFD showed in Figure 4.5 was further developed to study equipment sizing and process dynamics, generating the detailed engineering PFD of Figure 5.1. It was possible to obtain a simulation that converged in all three modes of SimCentral, thus, in theory, allowing for the dynamic response evaluation.

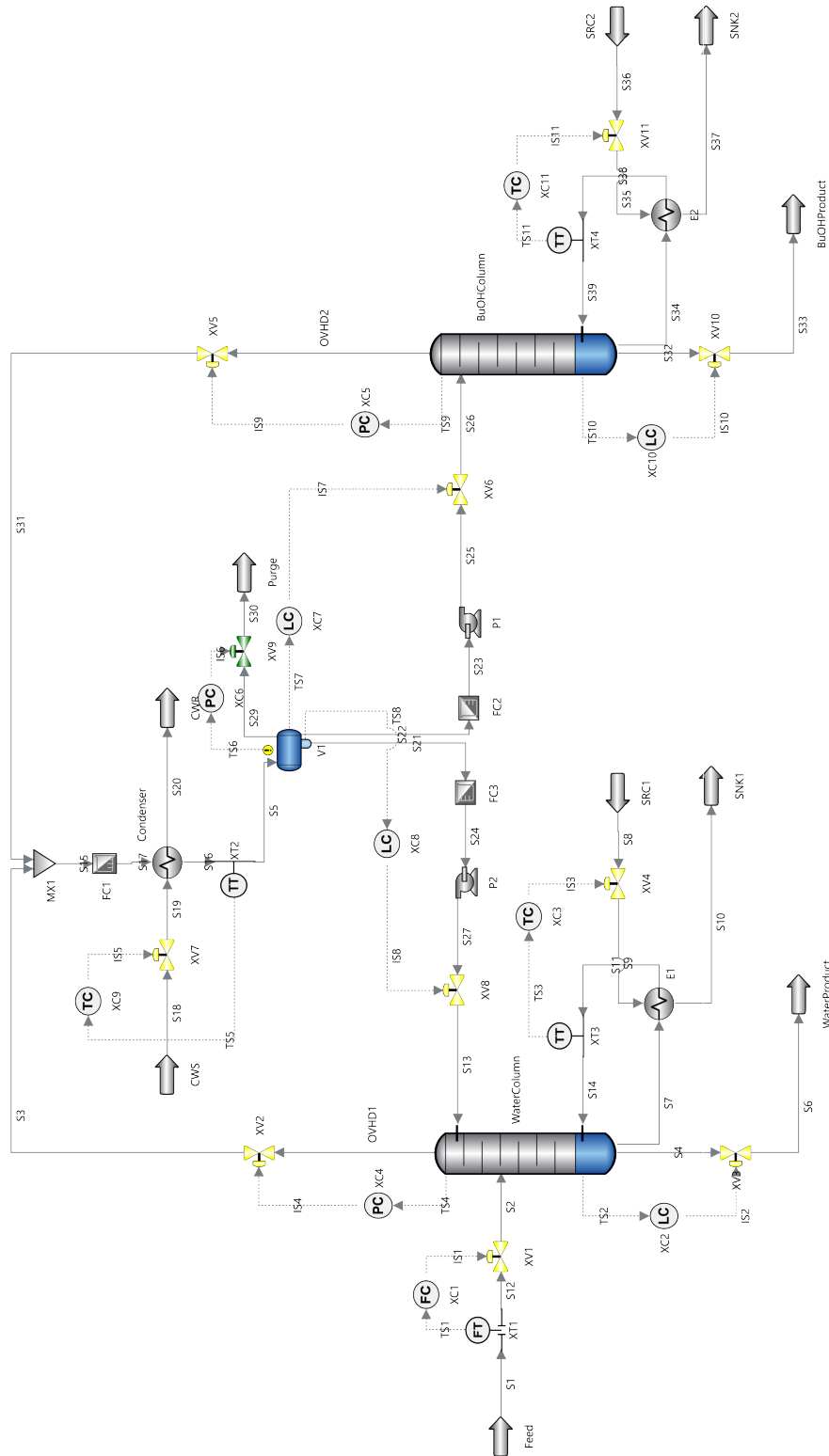


Figure 5.1: Detailed engineering PFD of water butanol separation process in SimCentral.

5.1.1 Fluid Flow Simulation

The SimCentral Simulation Platform uses the pressure-driven approach for the Fluid Flow and the Dynamics Modes. The Fluid Flow mode is actually a pressure-driven steady-state simulation, where the process is solved as a pressure network. Firstly, it is useful to rating and sizing of equipment, because pressure drops are evaluated. Secondly, it provides an intermediate state that is pressure balanced, facilitating the conversion and start of a dynamic simulation.

The detailed engineering PFD includes the control scheme devised in section 3.4 and some adjustments necessary to converge the simulation in the pressure-driven modes. They were:

1. New Decanter size and organic phase level to satisfy the required Net Positive Suction Head (NPSH) of both pumps;
2. Valves downstream the pumps were turned into check valves (facilitates dynamic mode);
3. The first Fluid Change block had to be moved from *after* the condenser to *before* the condenser (probably related to VLE calculation issues);
4. Recycle blocks for the process side of reboilers could be removed.

While several and known methods are available for controller tuning, it was decided to base the tuning in similar systems found in literature (Luyben, 2008a; Patraşcu *et al.*, 2017), simplified tuning rules (Skogestad, 2001) and in general control good practices for distillation columns (Skogestad, 2007).

An “engineering” approach was used to determine the pressure drops of the control valves that had to be specified, i.e. choosing a realistic pressure drop, that fits the overall pressure requirements of the process, and at the same time keeping the valve’s C_v within a reasonable range. In other words, ensuring that the valve is not too big, neither too small for the required

service. Some valves had their ΔP determined by the balance of pressure in the system; same case applies to the pumps.

5.1.2 Dynamic Simulation

Starting from a previously defined steady-state obtained in Process Mode (base case conditions), pressures are validated in Fluid Flow mode and the Dynamic Mode can then be started from this state.

Although the simulator indicates the initial state as “solved”, it was not possible to obtain results of scenarios of disturbances in the feed flow rate and feed composition. From the initial state it is possible to start the dynamic simulation and to introduce the disturbances. However, after some time, the simulation crashes.

There are a number of reasons why a dynamic simulation stops converging. The first one that was observed is an algorithm limitation, that is represented by deviations on the variables when starting from a steady-state result and without any disturbance. In this case, the calculation is simply a continuous validation of a previous, converged result. However, at some point one variable starts to deviate, leading to a chain deviations that eventually exceeds the tolerance for some variable, thus stopping the calculation.

This is a difficult error to prevent in the current version of the software, because the user has no access to the simulator’s solver tuning parameters (i.e. number of iterations, damping factors, tolerances, etc). Adjusting these parameters could allow for a solution of the scenario, at the cost of precision. Nevertheless, the overall dynamic behavior could be investigated.

The second reason observed is related to the hold-up times available throughout the process. In fact, in equipment where accumulation can occur (in this case, columns’ sumps and the decanter), the hold-up time plays a vital role in process dynamics. In SimCentral, the equipment cannot be defined in

terms of hold-up time, but only in terms of volume (via dimensions and/or level control). For example, when trying to run a scenario in dynamics mode and the simulation stops because the column went dry or the decanter is at maximum level, the only possible solution is to revert to process mode, play with the variables and retry dynamics. This makes the troubleshooting of the simulation a cumbersome process.

The third reason observed is related to process control. When running the scenarios, some variables had slower response than desired, while others reached the variation limits defined. This is the easiest problem to solve, as a simple adjust in the tuning parameters is sufficient to overcome the issue. However, sometimes problems can arise, such as control interference or snowball effects.

5.2 Equipment Sizing

Based on all the simulations and of the detailed analysis of the process, an initial sizing of the equipment for the process can be provided. These are not to be considered final design solutions, as process dynamics and cost optimization were not taken into account for the equipment sizing, which can affect significantly the results.

The sizes for the distillation columns are presented in Table 5.1. They are composed of the diameter as calculated by the tray sizing and rating tool of PRO/II, then inserted into SimCentral and validated through Fluid Flow Mode. The Heat Exchangers and the Decanter dimensions are the results of SimCentral, from detailed engineering simulation (of Figure 5.1), and are shown in Tables 5.2 and 5.3, respectively. Where indicated, materials of construction were considered for cost estimation purposes, as will be detailed in the next section, based on the chemical nature of the components.

Table 5.1: Distillation columns sizing

		Water Column	Butanol Column
Diameter	m	1,219	1,219
Height	m	5,9	5,9
# Trays	-	10	10
Feed Tray	-	5	1
Tray spacing	m	0,609	0,609
Tray type	-	Sieve	Sieve
Material	-	Stainless Steel	Stainless steel

Table 5.2: Heat Exchangers sizing

		Reboiler Water Column	Reboiler Butanol Column	Condenser
Surface	m^2	3298	3554	1230
Type	-	Floating head	Floating head	Floating head
Material	-	Stainless Steel	Stainless Steel	Stainless Steel

Table 5.3: Three-phase separator (decanter) sizing

Diameter	m	2
Length	m	5
Boot diameter	m	1
Boot length	m	1
L/D	-	2,5

5.3 Cost evaluation

To conclude the evaluation of the azeotropic distillation section for an ABE Plant, it is worth to briefly estimate the investment involved for the selected design. While a complete conceptual design will not be developed, the CAPital EXpenditure (CAPEX) and the OPERational EXpenditure (OPEX) of the main units —the two distillation columns with respective reboilers and the condenser —will be assessed, as well as the Total Annual Cost (TAC). The decanter and pumps costs are marginal compared to the main equipment and are, therefore, neglected.

On the one hand, Capital Expenditure is the sum of purchase and in-

stallation costs of an equipment. It is a value that is amortized during the plant's useful lifetime. Operational Expenditure, on the other hand, is the sum of the costs directly proportional to the operation of the plant —i.e. raw materials and utilities. The sum of these two quantities forms the Total Annual Cost (TAC) and provide an idea of the required investment to build and operate a process.

Among the possible methods for CAPEX estimation, Guthrie's method (Guthrie, 1969) is one of the most used. It provides a simple solution to estimate costs based price databases, characteristic dimensions of equipment and the use of economy of scale. There are several price databases available, among which two of the most known are *Marshall & Swift* (M&S), used on Guthrie's method, and the Chemical Engineering Plant Cost Index (CEPCI).

The generic equation of Guthrie's method is:

$$CI = a\left(\frac{M\&S}{280}\right)L_1^b L_2^c d \quad (5.3.1)$$

where CI is the cost of investment/installation in US dollars; “a” is a cost index, attributed according to the equipment type; “b” and “c” are the scale factors; M&S is the Marshall and Swift index at present time; 280 is the Marshall and Swift index in 1969; L_1 and L_2 are two characteristic dimensions of the equipment in consideration (only one may be sufficient); “d” is a term that takes into account the working pressure, the construction material and equipment type.

The parameters used in the present evaluation for CI calculation are shown in Table 5.4. The factors that affect the d term are: material of construction (Fm), working pressure (Fp), exchanger type (Fd), tray spacing (Fs) and tray type (Ft). Each equipment type has a final factor (Fc), calculated according to the method. The factors' values for the selected equipment and material (as in section 5.2) are reported in Table 5.5.

The OPEX can be assessed by direct calculation of required utility multiplied by the cost of utility. For heat exchangers, the duty is proportional to

Table 5.4: Parameters of Guthrie's method for the selected equipment (M&S index of 2018 is considered in all cases)

Parameter	Unit	Column (vessel)	Trays	Heat Exchanger
M&S	*	1638,2		
a	-	101,9	4,7	101,3
L_1	ft or ft^2	D	D	A
b	-	1,066	1,55	0,65
L_2	ft	H	H	-
c	-	0,802	1	-
d	-	2,18+Fc	Fc	2,29+Fc

Table 5.5: Factors for d term of Guthrie's method

Factor	Column (vessel)	Trays	Heat Exchanger
Fm	3,67	1,7	3,75
Fp	1	-	0
Fd	-	-	1
Fs	-	1	-
Ft	-	0	-
Fc	FmFp	Fs+Ft+Fm	(Fd+Fp)Fm

the utility (cold water or steam) as:

$$Q_C = UA\Delta T_{LM} = \dot{m}C_p\Delta T \quad (5.3.2)$$

$$Q_R = UA\Delta T_{LM} = \dot{m}\Delta H_L \quad (5.3.3)$$

where \dot{m} represents the mass flow rate of cooling water or steam and ΔH_L the latent heat (for steam). Since the CAPEX is expressed in US dollars, for the sake of coherence the utility cost considered is also expressed in US\$/GJ.

Eventually, the TAC is calculated from the following expression:

$$TAC = OPEX * t + \frac{CAPEX}{plantlifetime} \quad (5.3.4)$$

where t is the annual operation time of the plant. A typical operation time of 8000 hours per year, and a plant lifetime of 10 years is considered.

With the results from detailed engineering simulation in SimCentral, the utility consumption could be estimated and the costs of the design calculated, as summarized in Tables 5.6 to 5.8. The proposed design has a Total Annual Cost of 1,44 million dollars, for the considered plant lifetime. As can be observed from Table 5.6, the cost of the heat exchangers are by far the most relevant. It justifies the process optimization based on required duties as conducted in sections 4.4.3 and 4.4.2. Furthermore, it proves the potential to make the process more competitive by exploring intensification and integration.

Table 5.6: Detailed CAPEX for the azeotropic distillation of water-butanol

Water Column	Vessel	\$ 164.551,66
	Trays	\$ 12.319,42
	Reboiler	\$ 1.768.706,29
Butanol Column	Vessel	\$ 2.649,66
	Trays	\$ 12.319,42
	Reboiler	\$ 1.768.706,29
Condenser		\$ 931.474,26

Table 5.7: Detailed OPEX for the azeotropic distillation of water-butanol

		Reboiler Water Column	Reboiler Butanol Column	Condenser
Duty	GJ/h	6,53	8,56	4,15
Cost CW/Steam	1/GJ	7,78	7,78	0,72
OPEX	US\$/h	50,8	66,6	3,0

Table 5.8: Estimated Total Annual Cost for the azeotropic distillation of water-butanol

Total CAPEX	US\$, million	4,75
Total OPEX	US\$/h	120,39
Operating hours	year-1	8000
Plant lifetime	years	10
TAC	US\$, million	1,44

Finally, it is worth to remark that the reported TAC is just a preliminary estimation of the investment of the process for azeotropic distillation of water and butanol. A more detailed investigation can be performed by means of an optimization problem, where the TAC is the objective function to be

minimized. As the TAC considers not only the process, but also CAPEX, the optimum result may lead to improved process parameters as well. However, a global optimum is not guaranteed, as this is a typical non-linear optimization problem, that is likely to have multiple local optimal solutions.

Chapter 6

Conclusions

In the present MSc. thesis work, a process for the azeotropic distillation of water and butanol was developed, exploiting the phase separation promoted by the liquid-liquid equilibrium of the heterogeneous azeotrope. The process was validated and optimized through stationary simulation, while the final equipment sizing was verified by pressure-driven simulation. In addition to a traditional simulator, a novel software, capable of simulating in different modes, was used in the evaluations.

It is clear from the theoretical background and practical experimentation, that process thermodynamics play a very important role in distillation. It is even more sensitive when VLLE phenomena is involved, because of the higher complexity of the models. In fact, the correct composition calculation and phase definition within the simulation are of paramount importance for the convergence of the flowsheet. It was observed that, by allocating the phases correctly and using specific simulation strategies, the chances of convergence are increased, and computational effort is reduced.

Steady-state simulations of the proposed process for separation were successfully obtained in the simulator PRO/II, allowing the verification of energy and mass balance for a broad range of butanol fraction in the feed. The temperature, composition and flow profiles of the columns were obtained and commented, as well as the butanol recovery.

The simulations were used to investigate the energy requirement of the three heat exchangers that compose the process, as function of feed composition and for activity coefficient models. The results, when compared to the literature, confirmed that the process was correctly simulated.

The design was optimized by means of a sensitivity analysis of:

- Butanol fraction in the feed;
- The number of trays in each column and their pressure.

The best design was chosen in the basis of the duties involved, and the results showed how the energy demand in the columns changes as the butanol fraction is increased, corroborating the previous analysis of the heat exchangers.

The simulation was also successfully implemented in SimCentral, a novel simulation platform, capable of switching on-the-fly among different simulation modes. The results of the steady-state simulation (Process Mode) were successfully compared with those obtained in the other simulator, leading to the development of a full, detailed engineering simulation with control strategy for pressure-driven simulations.

The design was confirmed by the analysis in the Fluid Flow Mode of SimCentral, that considers the pressure nodes throughout the flowsheet. Some units had to be modified to cope with process dynamics. However, it was not possible to run scenarios of dynamic simulation in SimCentral, because the simulation would not converge when subjected to disturbances. This is related to simulator limitations with VLLE and variable adjustment.

To finalize the analysis of the process, a rough estimation of the process' Total Annual Cost was provided by means of Guthrie's method. Considering a plant lifetime of 10 years, the azeotropic distillation of water and butanol costs 1,44 million dollars per year to install and operate. This cost was not optimized and it does not take into account with any cost other than CAPEX and OPEX of the main units.

For future studies of this process the dynamic simulation can be further explored. Correct evaluation of the VLE and LLE phenomena can be assessed, as well as convergence strategies such as customizing the solver parameters and the hold-up volumes of the units. The verification of the response of the process to the disturbances can have an important effect in the design of equipment, eventually allowing the solution of the optimization problem of the cost estimation of the process and the definition of dynamic scenarios of start-up, shut-down and emergency response.

Bibliography

- Abdehagh, N., F. H. Tezel, and J. Thibault (2014). “Separation techniques in butanol production: challenges and developments”. *Biomass and Bioenergy* 60, pp. 222–246 (see p. 10).
- Bharathiraja, B., J. Jayamuthunagai, T. Sudharsanaa, A. Bharghavi, R. Praveenkumar, M. Chakravarthy, and D. Yuvaraj (2017). “Biobutanol—An impending biofuel for future: A review on upstream and downstream processing techniques”. *Renewable and Sustainable Energy Reviews* 68, pp. 788–807 (see pp. 5–7).
- Boffa, A. (2015). “La fermentazione acetone-butanolo-etanolo. Analisi e ottimizzazione dello schema di separazione”. MA thesis. Milan, MI: Politecnico di Milano (see pp. 11, 29, 31, 32, 38).
- Boutikos, P., C. S. Pereira, V. M. Silva, and A. E. Rodrigues (2014). “Performance evaluation of silica membrane for water–n-butanol binary mixture”. *Separation and Purification Technology* 127, pp. 18–28 (see p. 30).
- Buzzi-Ferraris, G. and F. Manenti (2012). “BzzMath: Library overview and recent advances in numerical methods”. In: *Computer Aided Chemical Engineering*. Vol. 30. Elsevier, pp. 1312–1316 (see p. 30).
- Chen, H., D. Cai, C. Chen, C. Zhang, J. Wang, and P. Qin (2019). “Techno-economic analysis of acetone-butanol-ethanol distillation sequences feeding the biphasic condensate after in situ gas stripping separation”. *Separation and Purification Technology* 219, pp. 241–248 (see p. 30).
- Cherubini, F. (2010). “The biorefinery concept: using biomass instead of oil for producing energy and chemicals”. *Energy conversion and management* 51.7, pp. 1412–1421 (see pp. 2, 4).
- Da Silva Trindade, W. R. and R. G. dos Santos (2017). “Review on the characteristics of butanol, its production and use as fuel in internal combustion engines”. *Renewable and Sustainable Energy Reviews* 69, pp. 642–651 (see p. 6).

- Di Pretoro, A., L. Montastruc, F. Manenti, and X. Joulia (2020). “Exploiting Residue Curve Maps to Assess Thermodynamic Feasibility Boundaries under Uncertain Operating Conditions”. *Industrial & Engineering Chemistry Research* (see p. 29).
- Di Pretoro, A. (2017). “Dynamic simulation and plantwide control of an ABE/W separation plant”. MA thesis. Milan, MI: Politecnico di Milano (see pp. 12, 27, 38).
- Douglas, J. and M. Douglas (1988). *Conceptual Design of Chemical Processes*. Chemical engineering series. McGraw-Hill (see p. 20).
- Dumitrescu, A. M., I. Banu, and G. Bumbac (2019). “Process modeling and simulation for butanol removing from fermentation broth by extraction with biodiesel”. *Renewable Energy* 131, pp. 137–143 (see p. 30).
- Errico, M., E. Sanchez-Ramirez, J. J. Quiroz-Ramirez, J. G. Segovia-Hernández, and B.-G. Rong (2016). “Synthesis and design of new hybrid configurations for biobutanol purification”. *Computers & Chemical Engineering* 84, pp. 482–492 (see p. 30).
- Gai, H., K. Lin, Y. Feng, M. Xiao, K. Guo, and H. Song (2018). “Conceptual design of an extractive distillation process for the separation of azeotropic mixture of n-butanol-isobutanol-water”. *Chinese Journal of Chemical Engineering* 26.10, pp. 2040–2047 (see p. 30).
- Garcia-Cano, J., M. D. Saquete, N. Boluda, and A. Houston (2018). “Experimental study of the LL, VL and VLL equilibria of water+ 1-butanol+ 2-octanol at 101.3 kPa”. *Fluid Phase Equilibria* 475, pp. 111–117 (see pp. 29, 30).
- Ginley, D. S. and D. Cahen (2011). *Fundamentals of materials for energy and environmental sustainability*. Cambridge university press (see pp. 1, 3).
- Gomis, V., A. Font, M. D. Saquete, and J. Garcia-Cano (2014). “Isothermal (liquid+ liquid) equilibrium data at T= 313.15 K and isobaric (vapor+ liquid+ liquid) equilibrium data at 101.3 kPa for the ternary system (water+ 1-butanol+ p-xylene)”. *The Journal of Chemical Thermodynamics* 79, pp. 242–247 (see p. 29).
- (2015). “Phase equilibria of the water+ 1-butanol+ toluene ternary system at 101.3 kPa”. *Fluid Phase Equilibria* 385, pp. 29–36 (see p. 30).
- Gorak, A. and Z. Olujic (2014). *Distillation: Equipment and Processes*. Handbooks in Separation Science. Elsevier Science. URL: <https://books.google.com.br/books?id=NwfUAgAAQBAJ> (see p. 23).
- Green, D. and R. Perry (2007). *Perry’s Chemical Engineers’ Handbook, Eighth Edition*. McGraw Hill professional. McGraw-Hill Education (see pp. 15, 38, 39, 42).
- Guthrie, K. (1969). *Data and techniques for preliminary capital cost estimating (chemical engineering, vol. 76)* (see p. 73).
- IEA (2019). *Renewables 2019*. <https://www.iea.org/reports/renewables-2019>. Accessed: 15/07/2020 (see p. 2).

- Kato, M., H. Konishi, and M. Hirata (1970). “New apparatus for isobaric dew and bubble point method. Methanol-water, ethyl acetate-ethanol, water-1-butanol, and ethyl acetate-water systems”. *Journal of Chemical and Engineering Data* 15.3, pp. 435–439 (see p. 29).
- Kister, H. (1992). *Distillation Design*. McGraw-Hill Education (see p. 16).
- Kister, H. Z. (1990). *Distillation operations*. McGraw-Hill, (see p. 33).
- Li, Y., W. Tang, Y. Chen, J. Liu, and F. L. Chia-fon (2019). “Potential of acetone-butanol-ethanol (ABE) as a biofuel”. *Fuel* 242, pp. 673–686 (see p. 8).
- Luyben, W. L. (2008a). “Control of the heterogeneous azeotropic n-butanol/water distillation system”. *Energy & Fuels* 22.6, pp. 4249–4258 (see pp. 27, 30, 55, 69).
- (2008b). “Comparison of Extractive Distillation and Pressure-Swing Distillation for AcetoneMethanol Separation”. *Industrial & Engineering Chemistry Research* 47.8, pp. 2696–2707. DOI: [10.1021/ie701695u](https://doi.org/10.1021/ie701695u) (see p. 24).
- Patraşcu, I., C. S. Bildea, and A. A. Kiss (2017). “Eco-efficient butanol separation in the ABE fermentation process”. *Separation and purification technology* 177, pp. 49–61 (see pp. 10, 27, 30, 69).
- Pereiro, A., J. Araújo, J. Esperança, I. Marrucho, and L. Rebelo (2012). “Ionic liquids in separations of azeotropic systems—A review”. *The Journal of Chemical Thermodynamics* 46, pp. 2–28 (see p. 24).
- Prausnitz, J., B. Poling, and J. O’Connell (2000). *The Properties of Gases and Liquids 5E*. McGraw Hill professional. McGraw-Hill Education (see pp. 19, 61).
- Qureshi, N., S. Hughes, I. Maddox, and M. Cotta (2005). “Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption”. *Bioprocess and biosystems engineering* 27.4, pp. 215–222 (see p. 11).
- Sánchez-Ramírez, E., J. J. Quiroz-Ramírez, S. Hernández, J. G. Segovia-Hernández, and A. A. Kiss (2017). “Optimal hybrid separations for intensified downstream processing of biobutanol”. *Separation and purification technology* 185, pp. 149–159 (see p. 30).
- Skogestad, S. (2007). “The Dos and Don’ts of Distillation Column Control”. *Chemical Engineering Research and Design* 85.1, pp. 13–23 (see p. 69).
- Skogestad, S. (2001). “Probably the best simple PID tuning rules in the world”. *Journal of Process Control* (see p. 69).
- Skogestad, S. and M. Morari (1988). “Understanding the dynamic behavior of distillation columns”. *Industrial & Engineering Chemistry Research* 27.10, pp. 1848–1862 (see p. 33).
- Stockhardt, J. and C. Hull (1931). “Vapor-liquid equilibria and boiling-point composition relations for systems n-butanol–water and isobutanol–water^{1, 2}”. *Industrial & Engineering Chemistry* 23.12, pp. 1438–1440 (see p. 29).

- Taylor, G. (2008). “Biofuels and the biorefinery concept”. *Energy policy* 36.12, pp. 4406–4409 (see p. 2).
- Van der Merwe, A., H. Cheng, J. Görgens, and J. Knoetze (2013). “Comparison of energy efficiency and economics of process designs for biobutanol production from sugarcane molasses”. *Fuel* 105, pp. 451–458 (see p. 30).
- Visioli, L. J., H. Enzweiler, R. C. Kuhn, M. Schwaab, and M. A. Mazutti (2014). “Recent advances on biobutanol production”. *Sustainable chemical processes* 2.1, p. 15 (see pp. 6–8).
- Xue, C., J.-B. Zhao, L.-J. Chen, F.-W. Bai, S.-T. Yang, and J.-X. Sun (2014). “Integrated butanol recovery for an advanced biofuel: current state and prospects”. *Applied microbiology and biotechnology* 98.8, pp. 3463–3474 (see p. 8).
- Yang, S.-T. and M. Yu (2013). “Integrated Biorefinery for Sustainable Production of Fuels, Chemicals, and Polymers”. In: *Bioprocessing Technologies in Biorefinery for Sustainable Production of Fuels, Chemicals, and Polymers*. John Wiley & Sons, Ltd. Chap. 1, pp. 1–26 (see p. 9).
- Yildirim, Ö., A. A. Kiss, and E. Y. Kenig (2011). “Dividing wall columns in chemical process industry: A review on current activities”. *Separation and Purification Technology* 80.3, pp. 403–417 (see pp. 24, 25).
- Yue, D., F. You, and S. W. Snyder (2014). “Biomass-to-bioenergy and biofuel supply chain optimization: Overview, key issues and challenges”. *Computers & Chemical Engineering* 66, pp. 36–56 (see p. 9).
- Zhu, Z., Y. Liu, and Y. Wang (2012). “Liquid–liquid equilibrium for the ternary system of 1-butanol+ 3-methyl-1-butanol+ water at different temperatures”. *Fluid phase equilibria* 335, pp. 14–19 (see pp. 29, 30).