



Valorization of by-products from bio-sources

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"You must be the change that you wish to see in the world."

M. K. Gandhi

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Abstract

The present thesis has the objective of studying the possible valorization of by-products from Amyris-Total farnesane production. This work was focused in the separation process development, through a process modelling using Aspen Plus v7.3 for the construction of a final process flow diagram and equipment design.

Wiped film evaporator and short path distillator equipments were used to perform the by-products separation. The separation was developed under vacuum conditions and using this type of evaporation equipment, due to the possibility of by-products thermal damage.

A preliminary cost estimation model was performed, including CAPEX and OPEX estimation. The main objective of the present study, was to obtain a first cost estimation to consider an extension of the farnesane production project which includes the by-products separation process.

There is a valorization opportunity for the by-products, since the obtained by-products bottom's price is greater than the price for farnesane diesel grade, so it means that a by-products separation process can be added to the existing process.

Keywords:

Valorization, by-products, farnesane, process development, cost estimation, Aspen Plus

Resumo

A presente dissertação teve como objectivo o estudo da possível valorização de sub-produtos da produção de farnesano da Amyris-Total. O trabalho foi focado no desenvolvimento do processo de separação, através da sua modelização utilizando o Aspen Plus v7.3, para a construção de um diagrama de processo e dimensionamento de equipamento.

Evaporadores de filme fino e de curto trajecto foram utilizados para a separação dos sub-produtos a valorizar. Devido à possibilidade de degradação térmica dos sub-produtos, o processo de separação foi desenvolvido sob vácuo e utilizando este tipo de equipamento de evaporação.

Executou-se um modelo preliminar de estimação de custos, incluindo a estimativa de CAPEX e OPEX. O principal objectivo do presente estudo foi a obtenção de uma primeira estimativa de custos para o projecto desenvolvido de forma a considerá-lo como uma possibilidade de extensão do processo de produção do farnesano existente em que se inclua o processo de separação dos sub-produtos.

Existe oportunidade para a valorização dos sub-produtos, uma vez que o preço obtido para a alimentação de sub-produtos é superior ao preço do farnesano classe diesel. Assim, o processo de separação de sub-produtos pode ser adicionado ao processo existente de forma a incluir a valorização desses.

Palavras-chave:

Valorização, sub-produtos, farnesano, desenvolvimento de processo, estimação de custos, Aspen Plus

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Abbreviations and Symbol List

Symbols

$\Delta P/\Delta z$	Pressure drop - distillation column
ΔP_p	Plate pressure drop
ΔP_s	Pressure drop in shell side
ΔP_s	Pressure drop in tubes side
ΔP_{pt}	Plates' ports pressure drop
ΔP_{pump}	Calculated pump head
ΔP_{total}	Total pressure drop
ΔT_{LM}	Logarithmic mean temperature difference
η	Efficiency
μ	Fluid dynamic viscosity
μ/μ_w	Dynamic viscosity term
ν	Kinematic viscosity
ρ	Fluid density in tubes/shell/plate/plate ports
ρ	Fluid density
$ ho_L$	Liquid density
$ ho_m$	Mixture density
$ ho_V$	Vapour density
$ ho_v$	Vapour density
A	Heat transfer area
$A_{schannel}$	Channel cross-sectional area
Cp	Specific heat capacity

D	Diameter
D_b	Tube bundle diameter
d_e	Hydraulic mean diameter
d_i	Tubes inner diameter
d_o	Tubes outer diameter
D_s	Shell diameter
D_V	Vessel inside diameter
F	F factor
F'	Capacity gas factor
F_v	Volumetric flow
F_{cu}	Cold utility mass flow
F_{hu}	Hot utility mass flow
F_{NG}	Natural gas mass flow
$F_{vliquid}$	Outlet liquid volumetric flow
$F_{vvapour}$	Outlet vapour volumetric flow
F_{vm}	Mixture volumetric flow
g	Gravity acceleration
G_s	Mass velocity
GHV_{NG}	Gross heating value of natural gas
Н	Height
H_D	Disengagement height
$H_D extra$	Extra height
H_H	Holdup height
H_S	Surge height
H_T	Total height
H_{LIN}	Height from HLL to the center of the inlet nozzle
H_{me}	Mist eliminator height
H_{roof}	Roofs' height

HLL	High liquid level
j_f	Friction factor
k	Thermal conductivity
L	Tubes length
L_p	Path length
M_{air}	Air molar mass
N_p	Passes number
N_p	Plates number
N_T	Number of tubes
$N_{tpasses}$	Tube passes number
NTU	Number of transfer units
P_v	Vapour pressure
P_{system}	System pressure
Q	Heat transferred
Re	Reynolds number
T_i	Inlet temperature
T_o	Outlet temperature
T_{cin}	Inlet cold fluid temperature
T_{cout}	Outlet cold fluid temperature
T_{hin}	Inlet hot fluid temperature
T_{hout}	Outlet hot fluid temperature
t_{holdup}	Liquid holdup time
t_{surge}	Liquid surge time
U	Overall heat transfer coefficient
u_p	Plate fluid velocity
$u_p t$	Plates' ports fluid velocity
u_s	Shell fluid velocity
U_T	Terminal velocity

u_t	Tubes fluid velocity
U_V	Vapour velocity
V_0	Elliptical head volume
v_v	Vapour velocity
$V_{cylinder}$	Cylinder liquid volume
$V_{equipment}$	Equipment total volume
V_{heads}	Heads liquid volume
V_{liquid}	Liquid volume
V_{os}	Oversized liquid volume
$V_{packing}$	Packing volume
V_{tank}	Tank volume
L/D	Ratio between height and diameter

Abbreviations

ASTM	American Society for Testing and Materials
BTL	Biomass To Liquid
CAPEX	Capital Expenditure
DC	Distillation column
EN	Energies Nouvelles
ET	Equalization tank
E	Heat transfer equipment
FSPD	FLASH for short path distillator
FWFE	FLASH - wiped film evaporator
GHG	Greenhouse Gases
HEFA	Hydrodroprocessed Esters and Fatty Acids
HETP	Height equivalent to a theoretical plate
INCOOLER	Internal condenser
MASS-B:F	Mass bottoms to feed ratio
MASS-D:F	Mass distillate to feed ratio

MOLE-D:F	Mole distillate to feed ratio
MSW	Municipal Solid Wastes
NPSH	Net positive suction head
OPEX	Operational Expenditure
RAMCEN	Rally Monte Carlo - Energies Nouvelles
RD	Reflux drum
RED	Renewable Energy Directive
RR	Reflux ratio
SPDINT	HEATER for intermediate short path distillator
SPDQINT	Intermediate short path distillator
SPD	Short path distillator
ST	Storage tank
TDE	ThermoData Engine
VLS	Vapour liquid separator
VP	Vacuum pump for vacuum ejectors
WFE	Wiped film evaporator

Chapter 1

Introduction

Nowadays, one of the most important world issues is the increasing of global energy demand, due to the economic growth and technological development seen over the last decades. According to Rabaey and Ragauskas [1], in 2050, the world economy will be four times larger than today and this growth will implicate an increase of 80% on total energy demand. Following this projections, there will be certain a boost on greenhouse gases emissions, namely in CO₂ emissions, contributing negatively to the global warming situation.

Contrary to what has been said, the petroleum resources are far from over, since it has been found new oil reservoirs over the last years. However, the crude oil quality is not as good as it was, and also its difficult accessibility, led to a constant need of improve the existing extraction and refining processes.

Attending to these environmental and technical-economic aspects, the use of renewable sources, as primary energy source, may harmonize the current situation, by using both fossil and renewable energy to produce heat, electricity and fuels for transportation sector. In 2035, the renewables should account for an average of 20% on global energy demand. This share is strongly dependent on the level of political actions, although, this general growth is normally related with financial support and rising of both fossil fuel and carbon prices. [2]

The use of biomass as a valuable feedstock to bio-products has a renewed interest due to some advantages, such as being a raw-material with a large availability worldwide, provide a secure energy supply for the future if used to produce biofuels or even give a new use to marginal lands by the development of energy crops. [3] In Europe, the implementation of RED directive, established a target of more than 10% of renewable energy in the final consumption for the transportation sector. [4]

Regarding the production of fuels and chemicals, the thermochemical and biochemical processes are the most relevant biomass conversion technologies. The thermochemical technologies are mainly applied to lignocellulosic biomass, due to their complex structure. This issue has been extensively studied in order to valorize the lignin, a by-product from the pre-treatment step applied to biomass 2G. [5] Concerning the scope of this dissertation, the fermentation process is the most relevant biomass conversion technology.

Through biotechnology it is possible to obtain bio-based hydrocarbons with similar properties to

fractions obtained from distillation of crude oil. In fact, the biotechnology approach has been made by metabolic engineering in microorganisms, like yeasts and bacteria. [6]

Some promising routes have been studied in this field, namely the isoprenoid-derived hydrocarbons, like farnesene from the sesquiterpene (C15) group. These hydrocarbons have attractive characteristics to replace jet-fuel and diesel from fossil sources. [6]

Total's mission is to provide energy-related products and services to meet the end costumers' needs, by going through hydrocarbon value chain, from discovery to commercialization, and also integrate the development of better energy for future, by exploring renewable energies, especially solar and also biomass. Total New Energies (EN) is then divided in two core sections: solar and biotechnologies. [7]

Solar is the most important business at Total EN. In 2011, Total became the majority shareholder of SunPower, holding 66% stake of the world's top solar company. With this partnership and other strategic approaches, Total aims to become a global benchmark in solar energy. [7]

In the biotechnologies, the main objective is to develop advanced bio-fuels and bio-molecules for transportation fuels and bio-chemicals. The goal for the next ten years is to have a commercial scale-up in biotechnologies, taking into account Total's markets needs.

Nowadays, the development is mainly centered in R&D and some partnerships, like Amyris-Total. Amyris engineers genetically modified yeasts capable to produce farnesene from sugar cane. In 2013, a commercial-scale production plant of farnesene started in Brotas, São Paulo, Brazil. Farnesene is hydrogenated into farnesane, which can be further blended into diesel and jet-fuel. However, the separation process of farnesane into carbon-fractions, like kerosene and diesel, is not completely optimized and there is a distillation column bottom of by-products. [8]

The present dissertation has the objective of studying the possible valorization of by-products from Amyris-Total farnesane production, following a common methodology for the creation of new products. This includes a process development, characterization of product samples and search of products applications and target markets.

However, this work was more focused on the separation process development, through a process simulation using Aspen Plus v7.3 for the construction of a final process flow diagram and equipment design. A preliminary cost estimation model was performed, since the main objective is to obtain a first cost estimation, in order to consider this hypothesis as an extension to the farnesane production project.

The present dissertation is organised in the following way: Chapter 2 presents a literature review on biomass, conversion technologies, biotechnology and introduction to the existing process from the Amyris-Total partnership, as well as the by-products to valorize. Chapter 3 a brief description of the common methodology followed to the creation of new products, from the process development to the cost estimation of the project. Chapter 4 describes the process modeling strategy and the validation of the obtained results against existing data collected by contracted companies. In Chapter 5, equipment design assumptions and procedures are detailed. Chapter 6 presents the preliminary cost estimation model explanation, comprising the analysis of the CAPEX, OPEX and total costs results and a conclusions about the by-products valorization opportunity. Finally, the Chapter 7 contains the main conclusions of the developed work and future work suggestions.

Chapter 2

State of the Art

In order to understand the basic concepts related to the scope of this work, a literature review was made focusing on biomass as a valuable feedstock to bio-products and their conversion technologies.

Regarding the purpose of this dissertation, within Total EN activities, it was made an approach to the use of biotechnology for the production of valuable products. An introduction to the process that was born from Amyris-Total partnership was also made, finishing with the by-products to valorize and the particular equipment used to perform their separation.

2.1 Biomass use as a source of energy

Over the last decades, a huge economical growth and technological development has been seen, which is leading to the crescent global energy demand. According to Rabaey and Ragauskas [1], in 2050, the world economy will be four times larger than today and this growth will implicate an increase of 80% on total energy demand.

On the other hand, the global warming concerns are real and such increase in global energy demand could lead to an unsustainable situation. The use of renewables is the most logical solution to harmonize global warming issues and mitigate GHG emissions, by using alternative sources to produce heat, electricity and fuels for transportation sector.

In 2035, the renewables will account for an average of 20% on global energy demand. This value is strongly dependent of political actions, although, this general growth is normally related with financial support and rising of fossil fuel and carbon prices. [2]

In the past years, solutions were developed for electricity generation from renewable sources, like wind and solar power, but the high consumption of liquid fuels from fossil sources is a remaining issue.

In Europe, some efforts have been made to harmonize this situation. The implementation of RED directive (2009/28/CE) is one of the tools to promote the utilization of renewable energy. For instance, it was established that, in 2020, each member state should account with more than 10% of energy from renewable sources in their energy final consumption in transportation sector. [4]

In fact, biomass-derived fuels are a starting point to accomplish RED directive goals, since they can

replace the conventional fossil fuels used for transports.

Biomass can be defined as the biodegradable fraction of products, wastes and residues that comes from agriculture, forestry and other related activities. The biodegradable fraction of municipal solid wastes (MSW) and algae are also included in this definition. [4]

A almost neutral carbon cycle can be obtained by using biomass as a source of energy products and chemicals. Plants naturally consume CO_2 to produce carbohydrates for their structural and natural needs. When any fuel is burned, the carbon source is oxidized to produce CO_2 and water. Since biomass is formed by carbon dioxide absorbed, the process is cyclical and replanted biomass will consume it for their natural growth. This cycle isn't fully neutral because there is some activities in biomass life cycle that also releases carbon dioxide to the atmosphere, for example, the machinery used in energy crops cultivation and the transport of biomass to processing units. [3]

Biomass is used since always, human kind begun to explore the energy content of biomass by burning it as a fuel for heating and cooking, as well as a food energy supply due to its nutritional content in sugars and starch.

Nowadays there is renewed interest in biomass as an energy source. Some of the drivers for biomass use are:

- Raw-material with a large availability worldwide, since it is also an indigenous resource;
- Application of biomass as a fuel may create a more secure energy supply for the future;
- · Production of biomass can generate more employment;
- Marginal lands can have a new use with energy crops. [3]

2.2 Biofuels generations

According to the definition given by RED directive, [4] a biofuel is a gaseous or liquid transportation fuel produced from biomass.

Biofuels are currently classified in three different generations, according to feedstock type and conversion technology.

2.2.1 First generation: 1G

First generation includes all biofuels produced from food crops - feedstocks that can be part of a food chain. The most common raw-materials included in this definition are: sugar cane, sugar beet, corn, wheat and vegetable oils from soybean, rapeseed, peanuts, palm and sunflower.

The production technologies for biofuels 1G are widely developed and most of then are now commercial, due to the easy accessibility and processing of feedstocks.

The most important first generation biofuels are bioethanol from corn or sugar cane and biodiesel from vegetable oils, like rapeseed or soybean. In 2011, the production of ethanol and biodiesel from rapeseed or soybean oils were 84.6 and 19.0 billion liters, respectively. USA and Brazil are the most important ethanol producers. [9]

There are some issues related with biofuels from edible sources that generates a general discussion inside industrial and social environment. These are related to their production costs and competition between land for energy or food purposes. [9]

2.2.2 Second generation: 2G

Second generation biofuels are those that are produced from lignocellulosic materials and other nonedible sources. These feedstocks are available in large quantities and in different types like: residues from wood industry, foresty and agriculture activity. There are also some special fast-grow cultures, like *myscanthus*, used to obtain a strong yield of biomass in a short period. [5]

Lignocellulose is composed by three polymers: cellulose, hemicellulose and lignin. These polymers form a complex and very strong three-dimensional structure.

The most developed liquid biofuels 2G are also bioethanol and biodiesel, as well as, synthetic diesel from hydrogenation of waste vegetable oils, like waste fried oils.

Biogas has already a large production, well established worldwide, through the anaerobic digestion of organic wastes and further methane capture, that has a high global warming potential but also high calorific value. [1] The biogas is usually produced from the organic fraction of MSW in landfills.

With regards to 2G sugar production, economic and technological constraints have been hindering their development of second generation biofuels. One of the most important reasons is the high cost of biomass and the fact that enzymatic hydrolysis process is expensive. These two aspects cover approximately 50% of the total production costs. [5] Regarding the technological issues, they are related with the complex structure of lignocelulosic biomass. Nowadays, biorefinaries use a pre-treatment step to breakdown lignocellulosic matrix in order to have access to simple sugars. This pre-treatment has a high energy consumption and should be optimized in order to reduce the costs associated to it. Lignin is a by-product in the conversion of lignocellulosic biomass into ethanol 2G. The use of lignin must be optimized to increase its value. It can be energetically valorized, to satisfy the production unit or used to manufacture several types of materials. [5]

2.2.3 Third generation: 3G

Third generation biofuels are normally associated to fuels obtained by CO₂ capture made by microorganisms activity, such as microalgaes.

In fact, biofuels derived from microalgaes are a auspicious subject, since these phototrophic microorganisms are able to produce and accumulate a large quantity of lipids only using sunlight as source of energy and carbon dioxide for carbon source. The capture of solar energy by microalgaes is 10 to 50 times more efficient than terrestrial plants. [10]

According to recent studies, the values for microalgaes biomass production are between 15 and 25 tonne/ha/year. This amount is higher than production of oil from common edible feedstocks. Microalgaes are one of the most promising biofuel feedstock, due to their environmental and technical benefits: fast growth rate, no land use, carbon sequestration and ability to accumulate high quantities of lipids. [10]

Just like other biofuels feedstocks, microalgaes have some weaknesses, mainly related to the vast energy input compared to the most common energy crops used for biofuels commercial production. Another aspect that must be considered is that there is still no existing standard method for an optimal lipid extraction applicable to all types of microalgaes. [10]

Essentially, production process of microalgaes biofuels should be simplified in order to avoid extensive energy input in the processing stages. Thereby, it should be possible to take advantage of the several benefits of microalgaes with fair price compared with equivalents from traditional pathways. [10]

2.3 Biomass conversion technologies

Biomass conversion technologies have been developed in order to obtain electricity, heat, fuels and chemical products from bio-sources, minimizing the actual impact of traditional technologies from fossil sources, commonly used to produce them.

The most ancient method is the direct combustion, in which biomass is burned inside a specific boiler in a oxidizing environment, producing high pressure steam that is used firstly to generate electricity and after as heating medium to processes and district heating. [11] There is also the traditional process of biodiesel production from the transesterification of vegetable oils, in which oil triglycerides reacts with a primary alcohol (like methanol or ethanol), with presence of basic or acid catalyst (depending of the feedstock acidity), to produce a mono-alkyl-ester (biodiesel) and glycerol, as a by-product.

Regarding the production of fuels and chemical products, the thermochemical and biochemical processes are the most relevant biomass conversion technologies. Among thermochemical technologies, there are some that can be highlighted, due to their extensive study and high future potential to obtain value-added products: pyrolysis, direct liquefaction, biomass-to-liquid (BTL). Concerning the scope of this dissertation, the biochemical processes are used, in particular fermentation.

2.3.1 Pre-treatment

Pre-treatment steps are often associated to biomass conversion technologies being applied to both biomass 1G and 2G. For biomass 1G, the most common pre-treatment is biological or chemical hydrolysis, using enzymes or acids, to convert polymers of stocked sugars in plants, like starch, to more simple sugars.

As can be seen in the figure 2.1, the biomass 2G (often denominated of lignocellulosic biomass), is constituted by two sugar polymers, cellulose and hemicellulose and a third one, lignin that gives structure to the plant tissues. In the case of biomass 2G, the sugar molecules are produced not for stocking sugar, but for the plant structural needs.



Figure 2.1: Lignocellulosic biomass structure. [12]

Lignin is one of the most abundant biopolymers, accounting for 20-25% in dry plant composition. As can be seen in the figure 2.1, a complex lignin network entraps polysaccharides, cellulose and hemicellulose, creating a barrier to their transformation to simple sugars. The immediate solution for lignin problem, which has been used in biorefinaries, is to submit the lignocellulosic biomass to a suitable pre-treatment, in order to promote the transformation of these sugar polymers to fermentable sugars. The most common pre-treatments are: milling, steam injection, temperature increase and solvent application. [13]

2.3.2 Pyrolysis

Pyrolysis is a process of thermal decomposition without presence of oxygen, from which can be obtained gaseous, liquid and solid products, wherein the proportion of each depends on the type of pyrolysis and operating conditions of the process. As can be seen in the table below, the temperature and residence time differs between 400 to 800° C and seconds to hours.

Pyrolysis	Temperature	Residence time	Liquid (% w/w)	Solid (% w/w)	Gaseous (% w/w)
slow	low (400° C)	high (hours)	30	35	35
fast	moderate (500° C)	low (\leq 2 s)	75	12	13
gasification type	high (800° C)	high	5	10	85

Table 2.1: Typical product yields and pyrolysis conditions, adapted from [14].

In the fast pyrolysis, it is obtained a high quantity of liquid product, bio-oil, whereas, in the slow pyrolysis there is a higher amount of solid product, biochar. In the gasification type, the main product is synthetic gas (or syngas), a mixture of CO and H_2 . Thus, for each type of pyrolysis there is always a product that is favored.

The most widely used process is fast pyrolysis, since the gases just have a few seconds of residence time in the reactor and works it with moderate temperatures. This process is also the one which produces more quantity of liquid product, being more interesting in view of their subsequent utilization for the production of fuels and chemicals. Fast pyrolysis requires a feed pre-treatment in order to allow a high rate of heat transfer in the reactor, avoiding a prolonged exposition to lower temperatures. A rigorous temperature control is also needed.

A pyrolysis bio-oil is a complex mixture of oxygenated hydrocarbons with some water that comes from the initial biomass moisture. The high content of oxygen is the main reason for its low calorific value, therefore, a large quantity of studies concerning bio-oils upgrading have been done, in order to achieve a higher combustion performance. [15]

2.3.3 Direct liquefaction

Biomass direct liquefaction is a type of hydrogenation process, at high pressure (100-200 atm) and moderate temperatures (400-600° C), from which can be obtained a liquid product. It's a one step process where the biomass is mixed with solvent using a specific catalyst.

The biomass is milled and mixed with water, with or without an additional solvent, forming a suspension with 10 to 30% of solids. This suspension is warmed until the reaction temperature, adding a reducer gas (H_2 or H_2 /CO) at high pressure and using a suitable catalyst. The yield of the direct liquefaction process depends of several parameters, for instance: temperature, pressure, biomass composition, type of solvent, catalyst used and residence time.

From this process is obtained a bio-oil with less oxygen than a pyrolysis bio-oil but with an higher viscosity. Having a lower content of oxygen makes this bio-oil more stable having less storage problems. However, this process is less attractive than pyrolysis, since the equipment is more expensive. [14]

2.3.4 BTL technologies

BTL technologies are essentially a set of two biomass conversion processes: gasification and Fischer-Tropsch synthesis.

Through the gasification process, biomass is converted into a combustible gas by partial oxidation (using steam, oxygen or a combination of both) of the feedstock at high temperatures (800-900° C). This gas mixture can be directly burned or used as a fuel for gas turbines in biomass integrated gasification/combined cycle. However, due to its low calorific value, it can have an extra value if used as a feedstock for the production of chemicals, instead of just being used as mentioned before. [3]

The synthesis of liquid products from synthetic gas is the well known Fischer-Tropsch process. In this process, the gas output from the gasification, a mixture of carbon monoxide and hydrogen (synthesis gas), is converted into a mixture of hydrocarbons chains, mainly long paraffinic chains, having also water as a by-product of this reaction. After, these hydrocarbons will suffer a hydrogenation or hydrocracking processes in order to obtain the desired hydrocarbon fraction yield.

To achieve a high efficiency in this step, the product selectivity should be promoted according to the desired output of the production plant. To accomplish that, an optimization of the catalyst and reactor performances should be made in a joint approach. [16]

2.3.5 Anaerobic digestion

Anaerobic digestion is a commercially proven conversion process in which organic matter is transformed into biogas, a mixture of methane and carbon dioxide. This process is very attractive, because it is a way to reduce greenhouse gases emissions, recovering energy in a form of a gaseous product with high energy content.

The biomass feedstock is degraded by bacteria in an anaerobic environment, producing a gas with an appreciable lower heating value compared with the feedstock used. Agricultural and agri-food wastes contain high levels of biodegradable materials, making them suitable feedstocks for anaerobic digestion.

The produced biogas can be purified into a high quality natural gas, removing the CO_2 , or it can be used directly in spark ignition gas engines and gas turbines to produce electricity. The capture of biogas is common in landfills, where the degradation of organic materials occurs in a natural way, avoiding methane emissions to the atmosphere. [3]

2.3.6 Fermentation

The fermentation concept may have an ambiguous definition, as it depends on its context of use. Considering a metabolic perspective, fermentation occurs in yeasts and bacteria for their natural needs.

In an industrial point of view, this process is used, since always, for production of alcoholic beverages and acidic products. Any industrial-scale process, in which microorganisms have a role in the transformation of sugar raw-material into chemical products, can be defined as a fermentation process in industry. A fermentation process is possible in aerobic or anaerobic environments. Microorganisms will choose naturally this path as long as sugars are available.

In biomass conversion, pre-treatment and hydrolysis steps are needed so that there is access to simple sugars for the fermentation process. This biomass conversion technology has a large use in the production of first generation bio-ethanol, produced from sugar and starch crops (sugar cane, sugar beet, corn...).

Several biotechnology studies have been done in order to optimize the production yield into the desired product from the fermentation process. The most common obtained-product is ethanol, since it is already naturally produced by yeasts and bacteria for their survival needs. However, as explained in the next sections, through metabolic engineering it is possible to have a production of other molecules from fermentation, using reprogrammed microorganisms. [3]

2.4 Biomass-derived jet-fuel

Attending to global warming situation it is urgent to reduce the global carbon footprint. The first step is the identification of the main CO_2 emission sources in order to promote reduction actions in the target CO_2 sources. In 2013, humans were responsible for the production of over 36 billion tonnes of CO_2 . In the same year, aviation industry produced 705 million tonnes of CO_2 - about 2% of human global CO_2 emissions. [17]

The use of biofuels for aviation industry can be a suitable alternative to reduce the impact of CO_2 emissions in the atmosphere. In fact, biojet derived from biomass can reduce the aviation fuel carbon footprint up to 80% in it full lifecycle. [17]

In a technical point of view, a biojet can be a substitute for the fossil jet-fuel since it is compatible with the actual engine fuel systems without any adaptation. For any biomass-derived jet-fuel, an ASTM international standards certification must be guaranteed for its use in the aviation industry. However, due to high jet-fuel quantities required and fluctuation of feedstock prices for its production, biojet is still an economically unfeasible option, even with technical approval according to the present infrastructures. [18]

Given the problematic between 1G, 2G and 3G biomass feedstock production, it must be given priority to non-edible oils for biofuels production, even if in a short term, the most readily available ones are edible oils from palm, soybean and rapeseed. Regarding the production of biojet, the most promising non-edible oily feedstock are: *Jatropha curcas*, *Camelina sativa*, *Salicornia bigelovii* and microalgae. [18]

Jatropha curcas is a small tree native from Central and South America. It can also be found in other tropical areas, such as India, Asia and Africa. Jatropha derived-oils have been promoted since it grows wild in poor soil in nutrients and water, so Jatropha growth as been considered an alternative to give a new purpose to non-used lands. Jatropha cannot be considered a real alternative for oil production, since research projects on relationships between farm methods and oil yields are limited, namely regarding land and water requirements. [18]

Camelina sativa is a plant which becomes mature 85 to 100 days after sowing having low water and fertilizer requirements while compared with other oilseed crops used in Europe. Due to its high seed oil content (about 40%), it has been studied as a potential feedstock for biofuels production. The USA military already did tests in their aircrafts using Camelina oil as jet-fuel. [19] [18]

Recently, *Salicornia bigelovii* as been considered as a potential non-edible oil crop, since it has up to 30% of oil in its constitution. This plant can grow in desert and even be irrigated with brackish water. [20]

As referred above, microalgaes derived-oils can be certainly used to produce biofuels due to its several advantages. However, both airlines and microalgae oil producers agrees that some factors such as rising oil prices, optimized biofuel yields and governmental support are necessary to bring this alternative to a commercial scale level. [18]

Nowadays, the leading process for renewable jet-fuel production is HEFA technology (Hydroprocessed Esters and Fatty Acids). This technology is adapted to several types of oil feedstocks and it is possible to integrate it in the actual crude oil refinery structure. The biojet produced using HEFA technology was already approved by ASTM, meeting all property requirements of ASTM D7566 (Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons). [18] [21]

UOP Honeywell Green Jet Fuel process, represented in the figure 2.2 bellow, uses HEFA technology. The process is divided in four steps (deoxygenation, separation, isomerization/hydrocracking and product fractionation) and besides green jet-fuel, other valuable by-products are obtained in the last separation step (green diesel, naphtha, LPG). This technology has a flexible feedstock since allows the process of a wide range of oils and fats. [21]



Figure 2.2: Process diagram - UOP Honeywell Green Jet Fuel. [21]

Within this technology, isomerization and selective catalytic cracking steps are critical for jet fuel production due to its specific properties. In fact, cold flow properties adapted to high altitude temperatures are extremely important so, it is necessary to have branched paraffins instead of linear ones which freezes when exposed to that temperature range. Selective catalytic cracking is preformed to obtain shorter-chain paraffins (between C7-C18), once jet fuel has a lower boiling point than diesel. [21] [18]

As described in the following sections, farnesane-derived jet-fuel production process is more simple than the UOP Honeywell Green Jet Fuel process, because farnesene is already a branched alkene with a number of carbons within the specified range for a jet-fuel. The Amyris-Total farnesane production process starts by sugar cane fermentation using engineered yeast strains, through metabolic engineering. These topics are further discussed in detail.

2.5 Biotechnology: a tool for biomass future

Biotechnologies can have an important role in the development of the energy supply for the future. In fact, through biotechnology, it is possible to obtain bio-based hydrocarbons with similar properties to fractions obtained from distillation of crude oil. As shown in figure 2.3, hydrocarbons between C5 to C23 can be used as transportation fuels and the development of bio-hydrocarbons has been focused in these specific fractions, since they have guaranteed markets.



Figure 2.3: Comparison between petroleum distillated fractions and bio-based hydrocarbons. [6]

A biotechnology approach used is metabolic engineering applied to microorganisms, such as microalgaes, bacteria and yeasts. Basically, the interesting pathways are selected and introduced into host organisms, producing genetically modified strains capable to generate desired hydrocarbons and bio-products. [6]

If the desired production yield is not achieved, a selection of metabolic pathways can be removed to promote the expression of the interesting ones. Even so, this manipulation should be performed while taking into account that some metabolic pathways are essential for microorganism survival and cannot be removed to correct the situation mentioned above. [22]

The study of microbial lipid metabolism and isoprenoid pathways are examples of metabolic engineering practices applied to the production of long and short chains of hydrocarbons. [6]

Microalgaes are specially known by their high lipid accumulation. These microbial oils may be an alternative to common oils used for the biodiesel production from edible feedstocks, avoiding "food vs. fuel" issues. [6]

Several studies have been performed regarding microalgaes' potential for the production of microalgaesbased biodiesel by an optimized production process. However, due to the lack of genetic manipulation tools, metabolic engineering studies on microalgaes are limited. [6]

On the other hand, a relevant number of yeast species is known for high production and accumulation of lipids if submitted to a suitable conditions (high carbon source and nutrient limiting environment). Metabolic engineering studies have been focused in *Yarrowia lypolytica* specie, due to the manipulation tools available for it. [6]

For both cases, additional *in vitro* processes (transesterification of oils fatty acids, for example) are needed to convert extracted lipids to diesel. A metabolic engineering challenge is to develop microor-ganisms capable of accumulate a high rate of lipids and convert them to diesel *in vivo*. In fact, due to the natural production of ethanol, yeasts are potential microorganisms for *in vivo* diesel production. [6]

Another promising route in this field, is the production of isoprenoid-derived hydrocarbons, more specifically monoterpenes (C10) and sesquiterpenes (C15), as substitutes for jet-fuel and diesel from fossil sources due to some of their properties (low freezing temperature and high ignition stability owing to their branched and cyclic carbon chains). [6]

Monoterpenes have been more used to flavors and fragrances applications. Even so, studies showed that saturated forms of myrcene and limonene can be a suitable additive for conventional diesel fuels. Metabolic engineering studies concerning monoterpenes and sesquiterpenes have been carried out by expression of *S. cerevisiae* mevalonate pathway in *E. coli*. [23] [6]

Regarding the production of short-chain hydrocarbons, it has been difficult to create replacement products for gasoline and bio-ethanol. The main reason for this delay is that microorganisms produce fatty-acids between C14 to C18 for natural structural needs, and this carbon chain length doesn't correspond to the desired target in short-chain hydrocarbons. [6]

There are some reports about the production of short-chain molecules using *E. Coli*, manipulated through metabolic engineering, however it is far from commercial applications, compared with isoprenoid route, namely with sesquiterpenes-derived fuels. [6]

Total New Energies has been working in several R&D projects and partnerships in order to identify and explore the most efficient technological paths to convert biomass into building block molecules to produce innovative solutions for transportation fuels and chemicals within the needs of other Total's markets. [8]

The main goal within biomass and biotechnology challenges is to achieve a biochemical platform capable to construct a "zero waste" process, where all the sugars in the carbon source are converted by fermentation into ethanol or other bio-molecules like derived-farnesene products. This process should also be economically feasible and good for the environment. Basically, the ideal scenario is to achieve a degree of development similar to the industrial corn ethanol production.
2.6 Process: Amyris-Total EN partnership

In 2010, Amyris and Total started a partnership for the development of biodiesel and biojet using farnesene produced by genetically modified *S. cerevisiae*. Concerning the scope of this dissertation, it is relevant to make an introductory approach to the process, from the feedstock processing to the final valuable products.

In the figure 2.4, it can be seen the simplified pathway of the conversion of fermentable sugars from sugar cane to produce farnesene, the "star" molecule from Amyris-Total partnership.



Figure 2.4: Biochemical pathways from sugar plants and starch under development at Total EN. Adapted from [8]

As common practice in any production unit, raw-materials are close to the processing plant. In fact, Brazil is the major and first producer of sugar cane, that is why the first commercial-scale production plant of farnesene is in Brotas, São Paulo. An efficient arrangement in a bio-production plant consists in a hybrid industrial plant that combines the "classic" processing of sugar cane with advanced fermentation processes to maximize raw-material's usage, gathering all the possible fermentable sugars into the fermentation process.

The sugar cane processing begins by loading and cleaning the harvested cane which is stored in large piles near the processing unit. These materials are crushed and milled in two main steps: breaking down the hard structure and grinding the cane. The first step involves the use of knives, crushers and shredders. For milling, it is common to use multi-steps roller mills. During the milling process, water or sugar cane juice, coming from other processing areas, are added to enhance juice extraction. This process is called imbibition. A portion of raw sugar cane juice is fed to the process of fermentation described below. The remaining raw sugar cane juice is then strained and clarified to obtain a clean liquid without solid particles that is fed into evaporators with multiple stages and submitted to other

operations to produce a raw crystallized product that is forwarded to refined sugar production unit. [24] In the figure 2.5 is represented a simplified flowsheet for farnesane production process from sugars, using yeast strains engineered using Amyris genetic engineering know-how.



Figure 2.5: Farnesane production process: Amyris-Total partnership - simplified flowsheet.

The first step is an aerobic fermentation process, where the "sugar feed", comprising sugar cane juice and molasse, is fermented by genetically modified yeasts into farnesene.

Amyris is a US start-up created in 2003 based on the research of Professor Jay Keasling in the expression of plant mevalonate pathway into microorganisms, like *S. cerevisiae*. This biotechnology platform is capable of engineering and screening yeast strains through an interactive screening process, where acquired knowledge is managed in order to have a continuous improving and a constant innovation in strain designs. [22]

Basically, a reprogrammed yeast has the genes that encode interesting cellular metabolic pathways, in this case mevalonate pathway that promotes the production of farnesene. Subsequent yeast strain generations were created with improvements in the production yield of desired molecules. [22]

After a scale-up process, the industrial plant in Brazil has nowadays several vertical fermenters with 200 m³ of volume each. Inside these equipments occurs a controlled aerobic fermentation process, from which is obtained a "soup" that is subjected to a separation process to remove water and remaining microorganisms. After an evaporation step, a distilled farnesene product it is obtained that is forwarded to a hydrogenation step.

Farnesene hydrogenation is made in Brazil via a simple batch process, a technology developed by Amyris.

Farnesene molecule, as an alkene with four unsaturations, is very reactive and suffers thermal degradation if stored before the hydrogenation process. The hydrogenation step is exothermic, with a high amount of released heat.

Total has been working in order to develop a continuous hydrogenation technology with suitable temperature control, using reactor technologies and catalysts already available in the market. In this way, some of the degradation reactions can be avoided or minimized, ensuring the quality of the hydrogenated product.

After the hydrogentation process, farnesane with quality diesel (farnesane D), is subjected to a dis-

tillation step in order to obtain farnesane K (kerosene grade). Farnesane can be directly blended into diesel or aviation fuels (jet A1) without any modifications in the current engines.

As well known, a jet fuel has very strict specifications, due to its adverse exposure conditions and also for safety reasons. In June 2014, farnesane biojet obtained a certification from ASTM to be used in commercial flights. After only three months, Total established a regular supply agreement with Air France, in order to prove that biojet can be industrially supplied to commercial airlines.

The commercialized biojet has an incorporation of 10% farnesane in the fossil jet fuel A1 and it is commercialized by Air Total International. Since January 2015, Air France does a flight Toulouse-Paris (Orly) per week, using the renewable jet fuel developed by the partnership Total-Amyris.

Farnesane D is being marketed by Amyris affiliates in Brazil, for supplying the transit authority of São Paulo with a blend containing more than 10% of farnesane. In the Monte Carlo New Energies Rally (RAMCEN) 2012, a 45% farnesane blend was used in real racing conditions, using a commercial vehicle. [8]

The objective of this dissertation was focused in the valorization study of the farnesane distillation column bottom, as can be seen in the figure 2.5. The distillation bottom comprises a remaining quantity of farnesane and by-products A, B and C. By-products were identified by letters according to an ascending boiling point order (by-product A is the most volatile after farnesane and C is the less volatile).

2.7 By-products separation: main equipment

The by-products may be susceptible to thermal degradation. To perform their separation, it is required to use adequate equipment performing a gentle distillation with a low thermal load.

For reducing the thermal damage, the evaporation temperatures must be lower, so this type of separation is performed under vacuum conditions, allowing a significant reduction when compared to the evaporation temperatures at atmospheric conditions. The residence time of the feed materials at evaporation temperature must be short, making a thin film evaporation an adequate method.

In this dissertation it were used two types of equipment - wiped film evaporator and short path distillator - which the basic principles are described in detail in the following sections.

2.7.1 Wiped film evaporator

The wiped film evaporators are appropriate for operating pressures between 1 mbar and 1000 mbar, in order to perform a gentle distillation of the feed materials. The residence time at evaporation temperature could be less than one minute.



Figure 2.6: Wiped Film Evaporator. [25]

As can be seen in the figure 2.6, the evaporation is done from a thin film (1 mm thick approximately) of feed materials created by a mechanical roller wiper system. The liquid is fed above and between the rotating distribution system and flows downward on the internal wall of the evaporator, while the volatile vapours from the film are led upwards being exhaust through the vapour nozzle. The evaporator is jacketed in order to perform the surface area heating using a heat carrier medium (normally heating oils or steam).

It is necessary to have an external condenser (partial or total) in order to condense the volatiles from the vapour nozzle. Usually, rectification columns are associated to this type of evaporators in order to achieve better results for the separation. In the latter case, the wiped film evaporator is working like a reboiler, since the vapour nozzle outlet stream is replacing the vapour outlet from a reboiler, as usually for a distillation column. [25]

2.7.2 Short path distillator

A short path distillator is used for operating pressures below 1 mbar and down to 0.001 mbar. The wiped film evaporator requires a certain pressure difference for transport of the formed vapours to the associated external condenser, so it cannot be used for this range of pressures. A short path distillator is the best choice when such low operating pressures are needed.



Figure 2.7: Short Path Distillator. [25]

In the figure 2.7, it can be seen an internal condenser in the center of the evaporator. The use of this range of pressures requires a minimized pressure difference between the evaporator and the condenser, so the vapours from the liquid film make a "short path" to hit the cold surface of the condenser. In this way, the required pressure difference is very low, since it is a short distance. The mechanical roller wiper system and the heating jacket work in the same way as the previous equipment. [25]

A molecular distillation takes place in a short path distillator. This fractionating process occurs at high vacuum, low temperatures and short residence times. In this process the vapour molecules can reach the internal condenser without intermolecular collisions and it is not possible return from the condenser to the evaporator. Thus, vapour-liquid phase equilibrium can not be reached. [26]

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Chapter 3

Methodology

The present work was inserted in a common methodology for the creation of new products. This includes a process development, characterization of product samples and search of products applications and target markets. Associated to a new product, there are also some regulations aspects that must be take into consideration within this methodology, namely for the transport and safety conditions.

A laboratory separation process for the by-products was developed for the purpose of having access to by-products samples and process operational parameters, which were guidelines for a process scaleup.

By-product samples were analyzed by a contracted laboratory. They were requested several types of analysis in order to collect relevant physico-chemical data to be presented to target-markets, selected by a business development team. For instance, for lubricants market kinematic viscosity is a determining property, so it was requested at various temperatures.

After feedback by product development teams of the target-markets, it could be necessary to request supplementary analysis or product samples to perform application tests. The next questions regarding a new product application is its price, availability and production volume.

The separation process development was made in three steps: process modelling, equipment design and cost evaluation.

The process modelling was made using Aspen Plus V7.3, a chemical process simulation program often used in process development. The process model was based on the laboratory separation process, including composition of the by-products feed, operational parameters and equipment sequence and arrangement.

The simulation was made for a by-products feed of 300 kg/h using a simplified composition determined by gas chromatography. This composition comprises farnesane and by-products A, B and C. Representative compounds from Aspen Pure Components Database were used. They were selected based in the molecular structure, molecular weight and boiling point.

Following the sequence of equipment used in the laboratory separation process, it was necessary to combine several Aspen blocks in order to model an wiped film evaporator and a short path distillator.

The wiped film evaporator was modelled using a HEATER followed by a FLASH2. Both equipments

were set for the same pressure, having each one a different function that combined made an evaporator. The HEATER was set for a vapour fraction close to 0.90, in order to simulate a moderate evaporation, since a wiped film evaporator is used for products susceptible of thermal degradation. The outlet stream from the HEATER is a vapour-liquid stream that is separated in a FLASH2. The rectification column associated to this equipment was modeled using a RADFRAC block without reboiler.

The short path distillator was modelled using both HEATER and a SEP2 blocks. The HEATER block was used to model the heat transfer to perform a moderate evaporation of the load and then to represent the internal condenser which was used for the condensation of load's lighter fraction. The SEP2 is a shortcut flash block, more simple that FLASH2 block, in which the separation is done by the specified fractions for the liquid and vapour outlet streams.

Based in the results of the separation process model simulation, the equipment design was made using appropriated handbooks to chemical engineering design problems.

The wiped film evaporator and short path distillator were designed in a simplified way, since it is a technology with protected intellectual property and know-how, developed by specialized companies. The design was based in the required heat and in an estimated overall heat transfer coefficient, in order to determine a heat transfer area. The vacuum systems must be designed in order to achieve the most economical solution, however, to simplify, it was made using a series of vacuum ejectors. The detailed sizing of each type of equipment is explained in the equipment design section.

The main objective of a separation process development and equipment design is to have a first cost estimation for this project. A cost estimation model was made, comprising the estimation of the capital expenditure (CAPEX), based in the cost of fixed assets and further improvements, and operational expenditure (OPEX), which includes the ongoing costs for the project.

It was also performed a case study model simulation using the bottom stream composition, flow, temperature and pressure from an existing simulation of the farnesane K (kerosene grade) distillation column, that is richer in farnesane than the composition used in the base case.

Chapter 4

Separation Process Development

A by-products separation process was developed based in a laboratory separation procedure described bellow. In this chapter are presented the process modelling strategy and simulation results for the base and study cases, developed using the Aspen Plus v7.3.

4.1 Laboratory separation process

A initial scheme for the by-products separation process was proposed by a contracted company. The separation was made using a laboratory/pilot scale process, where almost all the steps were in batch.

The initial feed was subjected to a batch distillation process performed in a existing industrial distillation column at 40 mmHg. The objective of this step was the recuperation of farnesane, with an adequate quality to be used in the production of biojet. Thus, it was obtained a distillation bottom richer in the by-products to valorize.

In the table 4.1, it is represented the simplified composition of the by-products feed determined by a gas chromatography. This was the start point composition for the process model simulations in Aspen Plus V7.3 (base case).

Component	Composition % (w/w)
Farnesane	12.6
By-product A	34.3
By-product B	47.5
By-product C	5.6

Table 4.1: By-products feed mass composition.

Evaporations were performed using a laboratory apparatus composed by an wiped film evaporator, a rectification column and an external total condenser. Both were carried out under medium-vacuum conditions, using operational pressures of 5 and 13 mmHg for first and second evaporation steps, respectively. In the second evaporation step takes place the separation between farnesane and by-product A. It was obtained by-product A, with a purity of 92 to 95% (w/w), as bottom product and a remaining farnesane quantity in the top.

The bottom stream from the first evaporation contains remains of the lighter components which are the cause for a low flash point of the by-product B. To obtain the desired flash point ($\ge 200 \circ C$), it was made an intermediate distillation step, using more intense vacuum conditions (P ≤ 1 mmHg), in order to remove these light components.

The by-product B was separated from the heavier components using a short-path distillator set for a pressure lower than 0.05 mmHg. This was a continuous step with the previous one, wherein by-product B outlet stream was filtered to remove vestigial solid particles.

4.2 Separation process modelling: Base Case

A separation process for the by-products feed was developed using Aspen Plus V7.3. Based in the feed composition presented in the table 4.1, it was considered 300 kg/h at the entrance of the separation unit. The system is under vacuum conditions, having more extreme vacuum in the separation of the heavier components.

4.2.1 Components and property methods selection

Representative conventional components were chosen to represent by-products B and C, since only farnesane and by-product A exist in the Aspen Pure Components Database. This selection was based in the chemical structure, molecular weight and boiling point of the true components.

Some differences between the boiling point of the true and representative compounds were verified. Nevertheless, the boiling point sequence remains the same.

In order to obtain the necessary transport and thermodynamic properties, two different Aspen Property Methods were selected for the model simulation: UNIFAC and MXBONNEL.

UNIFAC method is generally used for the estimation of the components missing properties by groups contributions. Group-group interactions are used to predict activity coefficients for vapour-liquid equilibrium. Therefore, it was used to complete pure components parameters, using the TDE estimation tool for the missing properties. [27, pg. 32]

MXBONNEL method is appropriate for vacuum systems, apolar components and uses Soave-Redlich-Kwong equations of state for the vapour-liquid equilibrium. The Soave-Redlich-Kwong thermodynamic method has good results for a wide range of components, considering the entire system is under vacuum conditions it was chosen this method. [27, pg. 65]

4.2.2 Modelling strategy and operating specifications

The by-products separation was made following the same sequence of the laboratory separation process. However, there are some differences between modelled and laboratory separation process, due to the fact that a continuous process was developed instead of a batch one.

A detailed description of the modelling strategy and operating specification results is presented in this section, based on the Aspen blocks arrangement methodology for each type of main equipment. The model flowsheet was divided in three sections, each one considering a separation step.

It should be noted that the sensitivity analysis presented does not account with columns pressure drop, that was inserted only in the simulation final stage. However, the operating specifications consider the updated pressure profile according to the pack sizing for each distillation column (see section 5.2).

Section B.1

Firstly, farnesane and by-product A were separated from the by-products B and C using a wiped film evaporator with a downstream rectification column and partial condenser, as shown in the figure 4.1.



Figure 4.1: Model process flowsheet: Separation of light and heavy components - Section B.1.

The Aspen blocks arrangement described in the methodology chapter for the wiped film evaporator (WFE-101 and FWFE-101) was used, followed by a RADFRAC column (DC-101) and a MIXER (ET-101) to connect the streams with the heavier components. This section was simulated using the same pressure of the first evaporation step in the laboratory separation process - 5 mmHg.

The vapour fraction specified in the HEATER block (WFE-101), allowed to achieve a C and B byproducts high recovery in the liquid stream from the FLASH block (FWFE-101), just dragging a vestigial quantity of farnesane and by-product A. The FWFE-101 outlet vapour stream was inserted on the last stage of the rectification column, initially set with ten stages, a total condenser and distillate to feed ratio of 50% (w/w).

A sensitivity analysis was made in order to obtain a similar temperature between the 5B1 and 6B1 streams. In fact, the 6B1 stream does not exist, since the bottom liquid is sent back again to the evaporator by the vapour nozzle. So, it was considered reasonable to have similar temperatures between

the exit streams of the FWFE-101 and the 6B1 stream. It should be noted that the temperature of the exit streams of the WFEF-101 is 218.4° C and maximum temperature difference of 2 to 3° C was considered as reasonable.

The manipulated variable was the mass distillate to feed ratio (MASS-D:F). The chosen outputs were the bottom temperature and recoveries for by-products B and A in the bottom, since they are the heavy and light keys of this separation, respectively. The sensitivity analysis results are shown in the table 4.2.

MASS D.E	Recovery 6B1	stream (w/w)	$6B1 \text{ etream} - T(^{\circ}C)$
IMA33-D.I	By-product B	By-product A	
0.4	1.000	0.354	147.8
0.425	1.000	0.294	150.4
0.45	1.000	0.235	153.8
0.475	1.000	0.175	158.7
0.5	1.000	0.115	166.4
0.525	1.000	0.056	181.4
0.55	0.987	0.010	217.0
0.575	0.929	0.010	217.0
0.6	0.870	0.009	217.1

Table 4.2: Sensitivity analysis results (DC-101) - MASS-D:F as manipulated variable.

Based on the main criteria mentioned above, the value of 0.55 was selected for the mass distillation to feed ratio. Furthermore, it was obtained a high recovery of by-products B and A in the bottom and top of the column, respectively.

The temperature profile was analyzed in order to conclude if all the specified stages were necessary to perform this separation, or if there are unused stages. In fact, has can be seen in the figure 4.2 a), there are five stages with a constant temperature of 261.5 ° C approximately. Thus, the same separation can be made having only five stages, which results in a distillation column with smaller height but the same performance.



Figure 4.2: Rectification column temperature profiles - DC-101.

Then, for having a continuous process, it was decided to change the total condenser for a partialvapour-liquid condenser, since a reflux is always necessary to have a regular and proper operation of the distillation column. In this way, it was possible to save a wiped film evaporator by introducing the top vapour stream (8B1) directly in the next distillation column, presented in the flowsheet section B.3.

The value for the mass distillation vapour fraction in the partial condenser was 0.995, thereby, the losses of farnesane and by-product A in the liquid distillate stream were minimum. This stream was joint with the heavier compounds streams (6B1 and 5B1) using a MIXER block set for the pressure of the

FLASH block presented in the flowsheet section B.2.

The operational specifications results for the flowsheet section B.1 are shown in the tables 4.3 and 4.4.

	WFE-101 (HEATER)	FWFE-101 (FLASH2)	ET-101 (MIXER)
Pressure (mmHg)	5.2	5.2	3
Heat Duty (kW)	-	0	-
Vapour fraction (molar)	0.9	-	-
Valid phases	Vapour-liquid	Vapour-liquid	Liquid only

Table 4.3: Operational specifications results for WFE-101, FWFE-101 and ET-101.

Table 4.4: Operational specifications results for DC-101.

Pressure (mmHg)	5
Stages	5 + Condenser
Condenser	Partial-Vapour-Liquid
Reboiler	None
MASS-D:F	0.55
Feed Stage	6
Distillate vapor	0.995
fraction (w/w)	

A pack sizing was performed in the RADFRAC block, according to method for the distillation column design. The pressure profile was updated accounting with the pressure drop in the column. For this reason, the wiped film evaporator (HEATER + FLASH2) pressure was changed for 5.2 mmHg. In the figure 4.3 it can be seen the updated temperature profile, accounting with the pressure drop over the distillation column.



Figure 4.3: Updated temperature profile - DC-101.

Section B.2

The separation of the heavier components was made using a vapour-liquid separator and short-path distillator to separate by-products B and C. The vapour-liquid separator was used to remove the remaining volatiles in order to obtain a by-product B flash point according to the target-markets requirements. The sequence of Aspen blocks used is represented in the figure 4.4.



Figure 4.4: Model process flowsheet: Separation of by-products B and C - Section B.2.

Several trials were performed to define the operating pressure for FLASH2 block (VLS-102). Starting with the pressure used in the laboratory separation process, a few values were tested evaluating the vapour stream output and the outlet liquid stream flash point. Trials results are shown in the table 4.5.

Pressure		2B2 Flash Point			
(mmHg)	Farnesane	By-product A	By-product B	By-product C	(° C)
1	0.254	1.508	22.079	0.808	219.9
1.5	0.246	1.411	10.805	0.356	218.4
2	0.232	1.257	5.523	0.173	216.2
2.5	0.213	1.071	3.116	0.096	213.7
3	0.190	0.876	1.885	0.057	211.1
3.5	0.162	0.683	1.168	0.035	208.6

Table 4.5: Trials for operating pressure selection - VLS-102.

The FLASH2 block (VLS-101) was set to 3 mmHg, considering that the loss quantity of by-products B and C in the 1B2 stream is low and the flash point in the liquid stream is closer to 210 $^{\circ}$ C.

The Aspen block arrangement described in the methodology chapter for the short path distillator (SPD-101, FSPD-101 and INCOOLER) was used. The operating pressure was set by the same ratio between flash and short path distillator in the laboratory separation process. Thus, the equipment was

set for a pressure of 0.15 mmHg ($P_{flash}/P_{SPD}=20$).

In the SEP2 block, standard split fractions were defined to perform the desired separation. A loss of 5% of by-product B was assumed for the residue stream and the same value for by-product C in the distillate stream.

To determine the required heat for the separation an intermediate short path distillator (SPDINT and SPDEQINT) was modelled. The HEATER block (SPDINT) was set to a vapor fraction of 0.90. Using the heat duty results of both blocks, a value of 3.7 kW was reached.

The Aspen block arrangement in the bottom of the figure 4.4 is the final flowsheet result, including pumps and heat exchangers to prepare the final products to storage (at 760 mmHg and 25° C).

The operating specifications concerning the main equipment of the flowsheet section B.2 are shown in the tables 4.6 and 4.7.

Table 4.6: Operational specifications results for VLS-102, SPD-101 and INCOOLER.

	VLS-102 (FLASH2)	SPD-101 (HEATER)	INCOOLER (HEATER)
Pressure (mmHg)	3	0.15	0.15
Heat Duty (kW)	0	3.7	-
Vapour fraction (molar)	-	-	0
Valid phases	Vapour-liquid	Vapour-liquid	Vapour-liquid

Table 4.7: Operational specifications results for FSDP-101.

Pressure	0.15	
Split fraction (defined to 10B2)	Farnesane	1
	By-product A	1
	By-product B	0.95
	By-product C	0.05

Section B.3

The separation of farnesane and by-product A is performed in this section, by using a RADFRAC distillation column block (DC-102). This column receives a vapour feed, comprising two streams, each one from a different flowsheet section. The Aspen blocks used are shown in the figure 4.5.



Figure 4.5: Model process flowsheet: Separation of farnesane and by-product A - Section B.3.

The equipment operating pressure was set to 3 mmHg. In this way, it was possible to recover the remaining farnesane and by-product A from the 1B2 stream, at the same pressure. The 1B2 and 8B1 streams were joint using a MIXER block set for 3 mmHg and were fed to the bottom of the column.

The 1B3 vapour stream was fed in the bottom stage of a distillation column with ten stages, a total condenser and without reboiler. Initially, it was set to a bottoms to feed ratio of 0.73.

Finally, a value of 0.80 was chosen for the bottoms to feed ratio specification. As can be seen in the table 4.8, the sensitivity analysis results leads to this value, since the recovery of by-product A in the bottom stream is high, as well as the purity of farnesane. The farnesane purity is above the specification for farnesane K - 98.88%, however the by-product A purity should be higher, since the desired value is between 92 to 95%.

	Recov	ery (w/w)	Mass purity (%)		
MASS-B:F	Farnesane (2B3) By-product A (3B3)		Farnesane	By-product A	
0.7	0.809	0.880	71.26	89.98	
0.73	0.800	0.918	78.35	90.08	
0.75	0.795	0.944	84.03	90.15	
0.8	0.756	1.000	99.98	89.50	
0.85	0.567	1.000	100	84.24	
0.9	0.378	1.000	100	79.56	

Table 4.8: Sensitivity analysis results (DC-102) - MASS B:F as manipulated variable.

To improve by-product A purity and adjust the farnesane outlet for the jet specification, a design analysis specification was performed. The desired farnesane purity (98.88%) was reached by manipulating the mass bottoms to feed ratio. In fact, using this tool, a purity of 90.3% was achieved for by-product A, only with a slight change in the mass bottoms to feed ratio value.

The column temperature profiles are shown in the figure 4.6. The temperature is stable around 116° C between the stages 8 and 11. Only one stage was removed, due to a significant difference in the

composition profile if more than one stage was eliminated. The updated temperature profile is on the right side of the figure 4.6 (b).



Figure 4.6: Distillation column temperature profiles - DC-102.

In order to consider a pressure drop profile in the column, it was necessary to change the equipment operating pressure, avoiding the use of a compressor at the entrance (if 3 mmHg were used as operating pressure for DC-102). The pack sizing was performed using the same values for the rectification column DC-101. It was set a condenser pressure of 2.5 mmHg. In the figure 4.7 it can be seen the updated temperature profile for DC-102 with 9 stages.



Figure 4.7: Updated temperature profile - DC-102.

At the end of the flowsheet section B.3, each one of the output product streams are prepared to be stored at 760 mmHg and 25° C, like in the previous section B.2.

The operating specifications concerning the present flowsheet section are summarized in the table 4.9.

Table 4.9:	Operational	specifications	results fo	or DC-102	and ET-101.

	DC-102 (RADFRAC)	ET-101 (MIXER)
Pressure (mmHg)	2.5	3
Stages	9 + Condenser	-
Condenser	Total	-
Reboiler	None	-
MASS B:F	0.79	-
Feed Stage	9	-
Valid Phases	Vapour-Liquid	Vapour only

4.2.3 Mass and energy balance

In this section the main stream results are presented, concerning mass and energy balance, obtained from the final model simulation.

It should be noted that, the compounds enthalpy reference state used by the Physical Property System of Aspen Plus V7.3 is the following: elements in their standard states at 1 atm and 25° C. This is the reason for negative enthalpy values. [27, pg. 7]

In tables 4.10, 4.11 and 4.12, are shown the component and total mass flow, temperature, pressure and enthalpy for the main process streams.

Mass Flow (kg/h)	1B1	5B1	4B1	6B1	7B1	8B1	9B1
Farnesane	37.80	0.06	37.74	0.18	0.02	37.54	0.26
By-product A	102.90	0.38	102.52	1.05	0.15	101.32	1.58
By-product B	142.50	34.77	107.73	106.34	0.53	0.86	141.64
By-product C	16.80	9.49	7.31	7.31	0.00	0.00	16.80
TOTAL	300.00	44.70	255.30	114.89	0.70	139.72	160.28
Temperature (° C)	25.0	219.3	219.3	217.9	145.9	145.9	218.0
Pressure (mmHg)	760	5.2	5.2	5.2	5	5	3
Enthalpy (kJ/kg)	-2079	-1107	-1471	-1359	-1802	-1907	-1291

Table 4.10: Mass and Energy Balance - Section B.1.

Table 4.11: Mass and Energy Balance - Section B.2.

Mass Flow (kg/h)	1B2	6B2	12B2	14B2	11B2	16B2
Farnesane	0.19	0.07	0.07	0.07	0.00	0.00
By-product A	0.89	0.71	0.71	0.71	0.00	0.00
By-product B	1.88	139.76	132.77	132.77	6.99	6.99
By-product C	0.06	16.74	0.84	0.84	15.91	15.91
TOTAL	3.01	157.28	134.38	134.38	22.89	22.89
Temperature (° C)	216.5	173.2	144.1	25.0	174.0	25.0
Pressure (mmHg)	3	0.15	0.15	760	0.15	760
Enthalpy (kJ/kg)	-1414	-1288	-1643	-1899	-392	-690

Mass Flow (kg/h)	1B3	2B3	6B3	3B3	7B3
Farnesane	37.73	29.53	29.53	8.20	8.20
By-product A	102.19	0.33	0.33	101.86	101.86
By-product B	2.74	0.00	0.00	2.74	2.74
By-product C	0.06	0.00	0.00	0.06	0.06
TOTAL	142.72	29.86	29.86	112.86	112.86
Temperature (° C)	147.5	90.8	25.0	115.8	25.0
Pressure (mmHg)	3	2.5	760	3	760
Enthalpy (kJ/kg)	-1897	-1901	-2048	-2363	-2568

Table 4.12: Mass and Energy Balance - Section B.3.

4.2.4 Separation process model validation

The model simulation results concerning the separated by-products outlets are shown in the table 4.13, including the total recovery, purity and flash point.

Component	Total Recovery (% w/w)	Purity (% w/w)	Flash Point (° C)
Farnesane	78.1	98.9	97.9
By-product A	99.0	90.3	119.3
By-product B	93.2	98.8	209.3
By-product C	94.7	69.5	231.4

Table 4.13: By-products outlets results - Base Case.

The separation process model validation was made by a comparison with the available data from by-product samples analysis and laboratory separation process. Due to confidential issues, only the strictly necessary analysis values are referred to perform this comparison.

As shown in the previous table (table 4.13), a high recovery was obtained for the three by-products. The recovered remaining farnesane is lower, probably due to their solubility in by-product A. However, a positive remark is that the jet specification was achieved for the recovered farnesane (farnesane K).

It was given priority to by-products A and B qualities, since these by-products have more potential to the target-markets than by-product C, because of its high viscosity. Thus, the main criteria to evaluate the by-products outlet were the purity and flash point for by-products A and B, respectively.

According to the available data, the by-product A purity must be between 92 and 95%. In the model simulation results, the maximum value obtained was 90.3%. As referred above, this value is due to the solubility of farnesane in by-product A. The purity could be reached if the volatiles stream (1B2) was not recovered however, the process development was performed by a "zero waste" approach.

For by-product B, the flash point must be greater than 200 $^{\circ}$ C, preferably about 210 $^{\circ}$ C. In this case, the obtained value meets the necessary requirements.

4.3 Process flow diagram

The process flow diagram shown in the confidential appendix was built from the separation process modeled using Aspen Plus v7.3. This diagram includes extra equipments which are not included in the simulation environment, but are needed in a real situation. For instance, the vapour-liquid separator (VLS-101) for the partial condenser, reflux drums (RD-101 and RD-102) and vacuum systems (VP). Coolers and storage tanks were also included for each by-product outlet.

4.4 Case Study

As mentioned above, the objective of the developed work is the by-products valorization from the residue of the farnesane K (grade jet) distillation column, through a separation process development. A case study was developed based in the residue feed flow and composition of the farnesane K distillation column. These data were obtained from an existing simulation and the main goal was to adopt the same process modelling strategy described above to perform the by-products separation and farnesane recovery.

Thus, the case study was developed based in the specifications and recoveries presented in the previous section and in the industrial distillation data from the laboratory separation process. In the case study simulation, the same Aspen Property Method and representative components were used, as specified above.

The pack sizing applied to the RADFRAC blocks was the same specified above for the base case. The reading of case study sections B.1, B.2 and B.3 should be done following the figures 4.1, 4.4 and 4.5.

The feed composition used is shown in the table 4.14. To simplify, a feed flow of 100 kg/h was considered. The temperature (280.7° C) and pressure (1275 mmHg) of the residue outlet stream were used as inputs for the case study.

Table 4.14: Feed mass composition - Case Study.

Component	Composition % (w/w)
Farnesane	86
By-product A	7
By-product B	5
By-product C	2

Section B.0



Figure 4.8: Case study flowsheet - Section B.0.

Considering this feed composition, it was necessary to model a distillation column to recover a significant amount of farnesane. In the laboratory separation process, a industrial distillation step was preformed with the same objective, so it was selected the same operating pressure (40 mmHg) for the recovery farnesane column simulation.

The modelling of distillation columns must be performed starting with shortcut blocks (DSTWU and Distl), in order to reach the optimized parameters for a rigorous distillation column block (RADFRAC). As can be seen in the figure 4.8, this approach was followed in the flowsheet section B.0. Firstly, DSTWU block was set to give the minimum reflux ratio value, based in the light (farnesane) and heavy (by-product A) key recoveries. It was assumed a loss of 5% of farnesane to the bottom stream. Several trials were made to achieve a distillate purity of 98.88%, by modifying the heavy key recovery.

The operational specification results for DSTWU block are shown in the table 4.15.

Pressure (mmHg)	40		
Minimum RR	0.579		
RR	0.695		
Light Key Recovery (%)	95		
Heavy Key Recovery (%)	12		
Stages	10 + Condenser + Reboiler		
Feed Stage	9		
MOLE D:F	0.862		

Table 4.15: Operational specification results - DSTWU block.

Secondly, using the previous results, it was used a Distl block in order to have a temperature estimation for top, bottom and feed stage. These temperature values were used to obtain the final temperature profile in RADFRAC block. The operational specification results for Distl block are summarized in the table 4.16.

Table 4.16: Operational specification results - Distl block.

Pressure (mmHg)	40		
RR	0.695		
Stages	10 + Condenser + Reboiler		
Feed Stage	9		
MOLE D:F	0.862		
Feed Stage T (° C)	152.6		
Top T (° C)	150.9		
Bottom T (° C)	171.5		

Finally, a distillation column RADFRAC block was set using the operating specifications obtained in the previous blocks. However, the temperature profile obtained was not regular and it had a significant perturbation in the feed stage, which reflected a temperature too high in the feed stream.

Thereby, it was used a HEATER block to cool down the feed stream in order to obtain a regular temperature profile according to the values obtained in the Distl block. In the table 4.17 are shown the operating specification results for the HEATER block.

Table 4.17: Operating specification results - Cooler (HEATER block).

Pressure (mmHg)	1275
T change (° C)	-100
Outlet T (° C)	180.7
Q (kW)	-8.8

To perform a final optimization of the RADFRAC block results, design specifications were carried out in order to obtain the desired purity (98.88 %) and recovery (95%) in the farnesene top stream, varying the reflux ratio and distillate to feed ratio, respectively.

The operating specification results for the RADFRAC block are summarized in the table 4.18, followed by the distillation column temperature profile (see figure 4.9) accounting with the pressure drop over the equipment (pack sizing tool).

Pressure (mmHg)	40			
RR	0.508			
Stages	10 + Condenser + Reboiler			
Feed Stage	9			
Condenser	Total			
Reboiler	Kettle			
MOLE D:F	0.863			

Table 4.18: Operating specification results - FaneDC (RADFRAC block).



Figure 4.9: Temperature profile - FANEDC.

As can be seen in the table 4.18, the reflux ratio obtained with the RADFRAC block is lower than the minimum reflux ratio obtained with DSTWU block (table 4.15). This result allowed to highlight the importance of following a sequence of distillation column blocks and achieve the final solution with a rigorous block, where it were obtained better operational specifications.

Section B.1

The feed mass composition in the case study section B.1 is quite different from the one used in the base case, as can be seen in the table 4.19. For this reason, it were obtained slightly differences in the operational parameters during the case study simulation, following the process modelling strategy explained above.

Table 4.19: Feed mass composition comparison in base and case studies - section B.1.

Commonant	Base Case	Case Study		
Component	Composition % (w/w)			
Farnesane	12.6	25		
By-product A	34.3	35		
By-product B	47.5	29		
By-product C	5.6	11		

The Aspen blocks arrangement for the wiped film evaporator modelling was set with the same operation parameters of the base case. Considering the values presented in the table 4.20, it were obtained similar recoveries between the feed and outlet vapour and liquid streams of the FWFE-101 (FLASH2 block). Even so, it can be noticed a higher recovery for by-products B and C in the liquid stream for the case study, which is a better result than having a higher recovery for the rectification column vapour feed stream.

Component	Base Case		Case Study	
Component	4 <u>B1</u> 3B1	<u>5B1</u> 3B1	4 <u>B1</u> 3B1	<u>5B1</u> 3B1
Farnesane	0.998	0.002	0.998	0.002
By-product A	0.996	0.004	0.997	0.003
By-product B	0.756	0.244	0.745	0.255
By-product C	0.435	0.565	0.431	0.569

Table 4.20: Recoveries comparison in base and case studies - FWEF-101 (FLASH block).

The rectification column DC-101 was simulated using the same pressure and distillate vapour fraction referred for the base case. However, the vapour feed flow is about 17 times less than in the base case, so several trials were made to achieve the adequate reflux ratio, in order to have comparable recoveries between the base and study cases. It was obtained a value of 0.40 for the mass reflux ratio, while in base case it was used a higher value - 0.56.

As can be seen in the table 4.21, similar values for farnesane and by-product A recoveries were obtained in the 8B1 stream for both cases. In the case study, the quantity of by-products B and C dragged in the 8B1 stream is lower than in the base case. This result can be clearly seen in the combined recovery of the 7B1 and 6B1 streams.

O a man a mant	Base	Case	Case Study	
Component	8 <u>B1</u> 4B1 <u>7B1+6B1</u> 4B1		8 <u>B1</u> 4B1	<u>7B1+6B1</u> 4B1
Farnesane	0.995	0.005	0.995	0.005
By-product A	0.988	0.012	0.988	0.012
By-product B	0.008	0.992	0.002	0.998
By-product C	4.94E-06	1.000	2.04E-06	1.000

Table 4.21: Recoveries comparison in base and case studies - DC-101 (RADFRAC block).

Section B.2

In the sections B.2 and B.3 it were found real differences in the operational specification between the base and study cases. It should be noted that the by-products final quality must be similar in both cases, so it was given priority to this aspect during the case study simulations in sections B.2 and B.3.

These differences are shown in the table 4.22 bellow, where it can be seen that the recoveries between base and study cases for VLS-102 (FLASH2 block) are different, since the simulation was focused in the optimum value for by-product B flash point.

In the FLASH2 block simulation it was necessary to change the operating pressure until reach the desired flash point for liquid outlet stream. After several attempts, the equipment was set to 2.2 mmHg

0	Base	Base Case		Study
Component	<u>1B2</u> 9B1	<u>2B2</u> 9B1	1 <u>B2</u> 9B1	2 <u>B2</u> 9B1
Farnesane	0.732	0.268	0.836	0.164
By-product A	0.554	0.446	0.692	0.308
By-product B	0.013	0.987	0.021	0.979
By-product C	0.003	0.997	0.006	0.994

Table 4.22: Recoveries comparison in base and case studies - VLS-102 (FLASH2 block).

of pressure, in order to to have a flash point closer to 211 $^\circ$ C.

The same approach was followed to set the pressure of the FSPD-101 (SEP2 block): a ratio of 20 between the pressure of the FLASH2 and SEP2 blocks. The operating pressure for FSPD-101 was 0.11 mmHg. The shortcut separation was performed according to the same split fractions given in the table 4.7.

Section B.3

In the section B.3, the distillation column DC-102 was set to a pressure of 1.7 mmHg (condenser pressure). The pressure profile was obtained from the same pack sizing tool input used in the distillation column simulations. Thereby, the pressure in the bottom stage is about 2.2 mmHg, which was the pressure set for the upstream MIXER block.

Apart from the operating pressure, the DC-102 (RADFRAC block) was initially set for the mass bottoms to feed ratio value used in the base case (MASS B:F=0.8). This value was modified by a design specification applied to this block, in order to reach the farnesane K grade purity. A value of 0.67 was obtained for the mass bottoms to feed ratio.

Analysing the table 4.23, it can be concluded that the vestigial amounts of by-products B and C in the by-product A output are similar, as well as, the recovered by-product A and farnesane in both cases.

0	Base C	ase	Case Study		
Component	2 <u>B3</u> 1B3	<u>3B3</u> 1B3	2 <u>B3</u> 1B3	<u>3B3</u> 1B3	
Farnesane	0.782	0.218	0.782	0.218	
By-product A	0.003	0.997	0.006	0.994	
By-product B	1.33E-31	1.000	4.55E-32	1.000	
By-product C	1.77E-31	1.000	1.74E-31	1.000	

Table 4.23: Recoveries comparison in base and case studies - DC-102 (RADFRAC block).

Separation process model validation

The case study simulation results concerning the separated by-products outlets are shown in the table 4.24, including the total recovery, purity and flash point.

Component	Total Recovery (% w/w)	Purity (% w/w)	Flash Point (° C)
Farnesane	78.1	98.9	97.9
By-product A	98.9	85.0	116.8
By-product B	92.9	97.2	206.7
By-product C	94.5	88.5	239.0

Table 4.24: By-products outlets results - Case Study.

High recoveries were obtained in both base and case studies. The obtained by-product A purity is lower than in the base case. It was obtained a value of 85.0% while in the case base the purity was 90.2%. The farnesane purity was specified by the design specification as 98.88%.

High purities were obtained for by-products B and C outlets: 97.2% and 88.5%, respectively. However. the by-product B flash point obtained (206.7 $^{\circ}$ C) was lower than the value in the base case (209.3 $^{\circ}$ C). This result can be explained by the fact that the separation was performed in a shortcut block, that could lead to erratic values, namely due to predicted values for transport properties.

The most significant differences verified between the base and study cases are in the operating specifications, namely in the DC-101 reflux ratio in the section B.1 and operating pressure in the sections B.2 and B.3.

Chapter 5

Equipment Design

In this section, the procedures for the equipment sizing are described, including the assumptions made to obtain the results for each equipment type. The main objective of the equipment design was to gather the necessary information for have a first cost estimation for the project, from the equipment price and utilities consumption.

5.1 Evaporation Equipments

The evaporation equipments comprise the wiped film evaporator WFE-101 and short path distillator SPD-101. Both equipments were sized using a similar and simplified methodology, since it requires technology expertise and know-how to perform a proper design.

The selection of an evaporator from a manufacture catalog is made based on the capacity and evaporator surface area required for the heat transfer process.

The evaporator heat transfer area was calculated using the general equation for heat transfer across a surface:

$$Q = UAF\Delta T_{LM} \tag{5.1}$$

Heating oils were used as hot utility, alternatively to high pressure steam, since they have an established temperature range, preventing an unstable evaporator operation. The heating oils temperature ranges between 300 and 200 ° C. To determine the hot utility flow, an average specific heat capacity of 2.72 kJ/kg K was used, calculated from a commercial heating oil data (see figure A.1).

Thus, an heat transfer area was determined based on the following assumptions:

- Overall heat transfer coefficient (U) was considered as constant over the evaporator. According
 to Chawankul et al. [28], the model developed shown better results using the measured U's from
 the experimental results than the predicted value from literature correlations, for the orange juice
 concentration;
- Estimated overall heat transfer coefficient from the figure A.2, based in the hot utility (heating oils) and process fluid (heavy organics/paraffins) types: U = 450 W/m²° C; [29, pg. 639]

• Factor F=1, since it was used a vapor fraction of 0.9, which was considered as in a phase change;

The internal condenser design is described in the heat transfer equipment section.

The design results for the evaporation equipments WFE-101 and SPD-101 are shown in the table 5.1, including the heat transfer surface and hot utility flow.

Equipment	WFE-101	SPD-101
Τ_{c in} (° C)	25.0	173.2
T_{c out} (° C)	219.3	173.9
Δ T _{LM} (° C)	121.8	64.1
Q (kJ/h)	198708	13248
A (m ²)	1.01	0.13
F _{h u} (kg/h)	731	49

Table 5.1: Evaporator equipments design results.

An heating oils recovery system was assumed, consisting in a fired heater which consumes natural gas to heat up the oil from 200 to 300 $^{\circ}$ C. [30, pg. 110]. From the total utility flow calculated, it was determined the amount of natural gas, by the ratio between the required heat and the natural gas calorific value (see table 5.2).

Table 5.2: Natural gas required to heating oils recovery system.

Total F _{h u} (kg/h)	779
Q (kJ/h)	211956
GHV _{NG} (kJ/kg) [31]	48848
F _{NG} (kg/h)	4.34

5.2 Distillation Columns

The distillation columns design was made for a structured packing type, often used for systems under vacuum. The most common packing was chosen, widely used for multiple applications in the chemical industry: Mellapak 250Y, manufactured by Sulzer.

The design was performed by the calculation of the diameter and height for the two equipments: DC-101 and DC-102. Both calculations were based on experimental data provided by the manufacturer, for the specific packing type (see figure A.3).

To obtain the hydraulics profile from the distillation columns model simulation, it was admitted a pressure drop by theoretical stage of 0.01 mmHg, since it is a medium vacuum system. [32, pg. 105] An average vapour mass flow and vapour density were obtained by the hydraulics profile output results.

The diameter calculation was performed by an iterative process, in order to obtain a minimal column pressure drop. The pressure drop can be read on the left side of the figure A.3 using the capacity gas factor (F'), calculated by the equation given bellow:

$$F' = v_v \sqrt{\rho_v} \tag{5.2}$$

The vapour velocity was calculated from the values of the average vapour mass flow, vapour density and column cross sectional area.

The height equivalent to a theoretical plate (HETP) was determined using a separation efficiency curve represented on the right side of the figure A.3. The total columns packed height was calculated by using the pack sizing tool in the distillation columns modeling, inserting the HETP and pressure drop values obtained by the packing manufacturer curves.

It should be noted that extra heights were considered of 1.2 m in the top, for vapour circulation and 1.8 m in the column bottom for liquid accumulation.

The distillation column results are summarized in the table 5.3.

Distillation column	DC-101	DC-102
Vapour Mass Flow (m ³ /h)	248.35	170.77
$ ho_{ m v}$ (kg/m³)	0.046	0.028
v _v (m/s)	3.37	4.41
F' (Pa ^{0.5})	0.73	0.74
HETP (m)	0.35	0.35
$\Delta \mathbf{P} / \Delta \mathbf{z}$ (mbar/m)	0.21	0.21
D (m)	0.75	0.70
H (m)	4.40	5.80
V _{packing} (m ³)	0.62	1.08

Table 5.3: Distillation column design results.

5.3 Heat Transfer Equipment

The heat transfer equipment designed includes condensers (total and partial) and heat exchangers to cool down the process outlet streams before storage.

The heat transfer equipment design is based on the heat transfer area calculation from the heat duty values obtained from the Aspen model simulation. The heat transfer area was calculated using the general equation for heat transfer across a surface, referred above in the evaporation equipment section.

Regarding the layout selection, shell and tube condensers and plate heat exchangers were considered, due to the small heat transfer surface obtained.

The design methodology and obtained results for condensers and heat exchangers are presented in the following sections, as well as, the design of the short path internal condenser, comprising only a bundle of tubes.

5.3.1 Condensers

Total and partial condensers were sized by the same procedure, since the vapour quantity in the partial condenser is greater that 70%, allowing a simple design based only in the forced convection heat transfer process. [29, pg. 720]

Cooling water was used as cold utility for condensers E-101, E-102 and SPD-101 internal condenser design. It was established a common temperature range for water cooled down in a cooling tower: 25 to 35 ° C. The cooling water average physical properties for this temperature range, are shown in the table A.1.

The heat transfer area was determined taking into account the following assumptions:

- An overall heat transfer coefficient value for vacuum condensers was selected: U=200 W/m² ° C;
 [29, pg. 637]
- The correction factor F was assumed equal to one since phase change occurs;
- The logarithmic mean temperature difference (ΔT_{LM}) was determined for countercurrent flow;

An overall heat transfer coefficient was not determined since the main objective is to have a simplified design to perform the project cost estimation, therefore a design approach based in a estimated U was considered adequate.

The main results concerning the heat transfer area calculations for condensers, including the required cooling water flow, are presented in the table 5.4 bellow:

A shell and tube condensers design starts with the fluids allocation. For a condensation process, phase change occurs in the shell and the cold utility flows inside tubes (dirtiest and higher pressure fluid). [29, pg. 659] A square pitch tubes arrangement was chosen, since the shell pressure drop is lower and it is easier to perform shell cleaning.

The shell and tube design was performed through a trial approach as usual for this type of equipments. Standard values for tubes length and diameter were used in the design procedure (see tables A.3 and A.2).

Condenser	E-101	E-102	SPD Internal
T _{h in} (° C)	204.0	91.3	173.9
T _{h out} (° C)	146.0	90.8	144.1
$\Delta T_{LM} (^{\circ} C)$	144.0	61.0	128.8
Q (kJ/h)	48387	52795	40399
A (m ²)	0.47	1.20	0.44
F _{c u} (kg/h)	1160	1265	968

Table 5.4: Heat transfer area calculation and utility consumption - condensers.

The main target for a shell and tube condenser design is to achieve typical velocity values inside shell and tubes, according to fluids allocation, by varying the available tubes length (L), outer diameter (d_o) , thickness and also the number of tube passes (shell passes are usually unitary).

For cooling water inside tubes, the typical velocities are in the range of 1.5 to 2.5 m/s, while for vacuum vapours in the shell the values must be between 50 and 70 m/s. [29, pg. 660]

The number of tubes (N_T) was determined by the following equation:

$$N_T = \frac{\pi d_o L}{A_T} \tag{5.3}$$

For the SPD internal condenser only a tube bundle was designed. To perform tube length selection, an L/D=3 was assumed for short path distillator dimensions. Thus, using the heat transfer area determined for the load evaporation it was concluded that the tubes bundle length must be lower than 0.65 m.

The tube bundle diameter (D_b) depends of the tube number and tube passes, since it will be necessary to leave some spaces to perform a proper accommodation of the tubes in order to have a desired flow pattern. The bundle diameter can be estimated using the equation given bellow: [29, pg. 648]

$$D_b = d_o (\frac{N_T}{K_1})^{1/n_1}$$
(5.4)

The constants used (K_1 and n_1) for this equation depends of the tube passes and were selected for square pattern (see figure A.5).

The shell diameter was determined using the figure A.4 by reading the minimum value for the difference between shell inside diameter and bundle diameter for a split-ring floating head type. No baffles were considered for both condensers (E-101 and E-102), due to the equipment small size.

Pressure drop in shell and tube sides (ΔP_s and ΔP_t) was determined through the following equations, respectively:

$$\Delta P_s = 8j_f(\frac{D_s}{d_e})(\frac{\rho {u_s}^2}{2}) \tag{5.5}$$

$$\Delta P_t = N_p [8j_f(\frac{L}{d_i})(\frac{\mu}{\mu_w})^{-0.14} + 2.5] \frac{\rho u_t^2}{2}$$
(5.6)

Viscosity and baffle spacing terms were not considered for shell pressure drop. As mentioned above, condensers sizing was performed without baffles and the viscosity term is not so relevant for a phase change phenomena. In the other hand, for pressure drop inside tubes there is an important temperature

fluctuation in the system, so it was accounted with the viscosity term, as correction to temperature effect.

The friction factors, j_f , were obtained by using the figures A.6 and A.7 for pressure drop inside shell and tubes, respectively. These values are dependent of the Reynolds number and a curve for 15% cut baffles was selected for shell friction factor reading. [29, pg. 720-725]

For shell pressure drop, the Reynolds number was calculated using an hydraulic mean diameter (d_e) and a mass velocity (G_s) . The mass velocity was determined using an average vapour flow rate, estimated according to the ratio between vapour in and out of the shell and the temperature profile for the partial condenser E-101 (see figure A.8). [29, pg. 672-675]

The condenser design results are shown in the table 5.5:

Condenser	E-101	E-102	SPD Internal
d _o (mm)	6.35	9.53	6.35
Thickness (mm)	0.71	1.24	0.71
d _i (mm)	5.64	8.28	5.11
L (m)	1.22	2.44	0.61
Pitch (mm)	7.94	11.91	7.94
NT	20	17	36
N _{t passes}	4	6	6
u _t (m/s)	2.7	2.4	1.8
D _b (m)	0.05	0.09	0.09
D _s (m)	0.10	0.15	
ΔP_t (bar)	0.672	1.014	0.238
$\Delta \mathbf{P_s}$ (bar)	0.007	0.003	_

Table 5.5: Condensers design results - shell and tube calculations.

5.3.2 Plate Heat Exchangers

Plate heat exchangers were designed following a procedure similar to the one described above for shell and tube condensers.

Chilled water was used as cold utility for cooling down the separation process outlet streams to 25° C, with a temperature range of 10 to 15° C. In this type of heat exchangers, low approach temperatures can be used, as low as 1° C. [29, pg. 754] The chilled water average physical properties, for the above-mentioned temperature range are shown in the table A.1.

The heat transfer area was obtained accounting with the following assumptions:

- An overall heat transfer coefficient value for heat transfer between viscous organics and cooling water in a plate exchanger was used: U=250 W/m²° C; [29, pg. 638]
- The correction factor F was determined for each case, assuming a pass arrangement 1:1 by the method referred in the appendix A.3;
- The logarithmic mean temperature difference was also determined for countercurrent flow.

The results concerning the heat transfer area calculation for plate heat exchangers, including the chilled water flow for each one are shown in the table 5.6:

Heat-Exchanger	E-103	E-104	E-105	E-106
T _{h in} (° C)	91.0	115.9	144.3	174.2
T _{h out} (° C)	25.0	25.0	25.0	25.0
ΔT_{LM} (° C)	38.0	45.0	53.0	61.0
Q (kJ/h)	4425	23141	34525	6846
A (m ²)	0.14	0.59	0.76	0.13
F _{c u} (kg/h)	212	1106	1650	327

Table 5.6: Heat transfer area calculation and utility consumption - plate heat exchangers.

The number of plates required for the heat transfer, as well as the flow arrangement and number of passes were determined. According to Sinnott [29, pg. 753], plates surface areas range from 0.03 to 1.5 m² with width to length ratio from 2 to 3. Plates are normally placed with a gap between 1.5 to 5 mm with a thickness from 0.5 to 3 mm.

A width to length ratio of 2, a gap between plates of 1.5 mm and a plate thickness of 0.5 mm were selected. The number of plates (N_p) were determined by dividing the total heat transfer area and the area of a plate. The number of channels per pass must be an even number so several plate width trials were performed in order to respect this condition and the plate surface range referred above.

The channel cross-sectional area ($A_{s \text{ channel}}$) and hydraulic mean diameter (d_e) were also determined using the value for the gap between plates. The values obtained were 0.0002 m² and 0.003 m, respectively.

Plate pressure drop (ΔP_p) was estimated using the following equation for flow in a conduit that was applied for each stream:

$$\Delta P_p = 8j_f(\frac{L_p}{d_e})(\frac{\rho {u_p}^2}{2})$$
(5.7)

The path or plate length (L_p) corresponds to the plate effective length that was determined by the width to length ratio mentioned above.

The friction factor (j_f) depends of the plate design and for a preliminary calculation it was determined by the following equation for turbulent flow.

$$j_f = 0.6Re^{-0.3} \tag{5.8}$$

According to Sinnott [29, pg. 758], the transition between laminar and turbulent flow often occurs between 100 to 400, even so, turbulence can be achieved at very low Reynolds numbers and this is the main reason which makes plate heat exchangers suitable for viscous fluids.

The pressure drop in plates' ports (ΔP_{pt}) was also determined based in the velocity through them. This value must also be added to the pressure drop refereed above. It was obtained using the following equation:

$$\Delta P_{pt} = 1.3 (\frac{\rho u_{pt}^2}{2}) N_p \tag{5.9}$$

The port diameter was considered as 20% of the plate width.

The plate heat exchangers design results are shown in the tables 5.7, 5.8 and 5.9, being the latter ones refereed to pressure drop calculations:

Heat-Exchanger	E-103	E-104	E-105	E-106
plate width (m)	0.125	0.150	0.150	0.125
plate length, L _p (m)	0.250	0.300	0.300	0.250
plate area (m ²)	0.031	0.045	0.045	0.031
port diameter (m)	0.025	0.030	0.030	0.025
Np	4	13	17	4
Channels per pass	2	6	8	2

Table 5.7: Plate heat exchangers design results - layout.

Table 5.8: Plate heat exchangers design results - pressure drop (chilled water).

Heat-Exchanger	E-103	E-104	E-105	E-106
u _p (m/s)	0.19	0.22	0.26	0.30
u _{pt} (m/s)	0.12	0.43	0.65	0.19
ΔP_p (bar)	1.15E-02	1.88E-02	2.36E-02	2.62E-02
ΔP_{pt} (bar)	9.64E-05	1.27E-03	2.83E-03	2.31E-04
ΔP_{total} (bar)	1.16E-02	2.00E-02	2.64E-02	2.64E-02

Table 5.9: Plate heat exchangers design results - pressure drop (process fluid).

Heat-Exchanger	E-103	E-104	E-105	E-106
u _p (m/s)	0.03	0.03	0.03	0.04
u _{pt} (m/s)	0.02	0.05	0.07	0.02
ΔP_p (bar)	5.71E-04	1.18E-03	9.25E-04	1.25E-03
ΔP_{pt} (bar)	2.53E-06	1.53E-05	2.49E-05	2.04E-06
ΔP_{total} (bar)	5.74E-04	1.20E-03	9.50E-04	1.25E-03

5.4 Vapour-Liquid Separators

Two vapour-liquid separators were sized for a phase separation by gravity action. Basically, it consists in a flash drum where the separation is performed due to a velocity decrease caused by an enlargement of the vessel cross section.

The sizing procedure described in this section was based in a technical article for design of twophase separators. [33]

A vapour-liquid separator can have a vertical or horizontal orientation. The vessel position depends of the ratio between the amount of gas and liquid. A vertical separator must be used to separate mixtures with a high vapour/liquid ratio, while the horizontal separators are preferred for the opposite case.

In the table 5.10 are shown the outlet vapour and liquid volumetric flows which were the orientation selection criteria for the vapour-liquid separators.

Separator	VLS-101	VLS-102
F _{v vapour} (m ³ /h)	3250	94
F _{v liquid} (m ³ /h)	0.106	0.237
Orientation	Vertical	Vertical

Table 5.10: Vapour-liquid separator orientation selection.

The vapour-liquid separator design started by the calculation of the terminal velocity (U_T) for liquid droplets settling, given by the following equation:

$$U_T = K \sqrt{\frac{(\rho_L - \rho_V)}{\rho_V}}$$
(5.10)

The separation K value was obtained from the literature. For both cases, it was used a value of 0.2. This value is for vapours under vacuum and with mist eliminator. The liquid droplets will settle down as long as the vapour velocity (U_V) is lower than the terminal velocity, so, for a conservative design it was considered $U_V=0.75U_T$.

The vessel inside diameter was determined from the following equation, using the vapour volumetric flow and vapour velocity:

$$D_V = \sqrt{\frac{4F_{vvapour}}{\pi U_V}} \tag{5.11}$$

Liquid holdup and surge times were selected from an existing table. [33] For the separator VLS-101, the selected values were suitable for a separator upstream of a distillation column (t_{holdup} =5 min and t_{surge} =3 min), while, for separator VLS-102, it was used the same holdup time and a surge time of 2 min. The holdup and surge volumes were determined using the previous values and liquid volumetric flow.



Figure 5.1: Vertical vapour-liquid separator. [33]

In the figure 5.1, the calculated heights are outlined. The low liquid level height (H_{LLL}) was selected from a table based in the separator diameter. [33] The holdup and surge heights (H_H and H_S , respectively) were calculated from the ratio between the volumes and the cross sectional area. The height from the high liquid level (HLL) to the center of the inlet nozzle (H_{LIN}), without inlet diverter, was given by:

$$H_{LIN} = 12 + 0.5d_N, (in) \tag{5.12}$$

The inlet nozzle diameter (d_N) was determined by the following equation:

$$d_N \ge \sqrt{\frac{4F_{vm}}{\frac{\pi 60}{\sqrt{\rho_m}}}}, (ft)$$
(5.13)

Where F_{vm} and ρ_m are the volumetric flow and density of the mixture, respectively.

The disengagement height (H_D) between the center of the inlet nozzle and the top of the vessel, with mist eliminator, was given by:

$$H_D = 24 + 0.5d_N, (in) \tag{5.14}$$

The total height of the vessel was determined by the sum of the several heights mentioned above, plus 0.15 m to mist eliminator and 0.30 m for an extra height in the separator top:

$$H_T = H_{LLL} + H_H + H_S + H_{LIN} + H_D + H_{me} + H_{extra}$$
(5.15)

The design results for the vapour-liquid separator VLS-101 and VLS-102 are shown in the table 5.11.

Separator	VLS-101	VLS-102
D (m)	0.60	0.22
H _H (m)	0.03	0.50
H _S (m)	0.02	0.20
d _N (m)	0.06	0.02
H _{LIN} (m)	0.34	0.33
H _D (m)	0.64	0.62
H _{LLL} (m)	0.38	0.38
H _T (m)	1.87	2.48

Table 5.11: Vapour-liquid separator design results.
5.5 Storage Tanks and Vessels

5.5.1 Storage Tanks

Three storage tanks were designed for by-products storage. It was considered that the raw-materials and farnesane storage tanks were already installed where the project will be established. The by-products were stored at atmospheric pressure and ambient temperature ($25 \degree C$).

The storage tanks can be horizontal or vertical depending of the liquid volume to storage [32, pg. 459]:

- Volume less than 3.8 m³ vertical tanks on legs;
- Volume between 3.8 and 38 m³ horizontal tanks on concrete support;
- Volume greater than 38 m³ vertical tanks on concrete foundations;

To choose the roof type for the storage tanks, it should be taken into account the possible losses by evaporation of the by-products. The criteria to select the most suitable roof type is based on the vapour pressure of the stored materials [34, pg. 144]:

- For vapour pressure less than 0.103 bar fixed roof;
- For vapour pressure greater than 0.103 bar but lower than 0.78 bar floating roof;

It was considered a residence time of 30 days for the storage. The liquid volume stored were determined by the product between the volumetric flow and the residence time. The obtained volume was 20% oversized.

For the tanks ST-101 and ST-102, the oversized volume was greater than 38 m³, so the tanks were vertical supported in concrete foundations. For by-product C tank (ST-103), the value was between 3.8 and 38 m³, hence an horizontal tank on concrete support was sized.

To obtain the tank diameter it was used a value for the ratio between the height and diameter (L/D) defined according to the oversized volume [35, pg. 627]:

- Volume less than 95 m³ L/D=3;
- Otherwise L/D=1/3

For tanks ST-101 and ST-102, it was used L/D=1/3, while for by-product C tank ST-103 the inverse value was used. The tank diameter was calculated using the following equation:

$$D = \sqrt[3]{\frac{4V_{os}}{\pi/3}} \tag{5.16}$$

To calculate the tank height it was included an extra height of 0.30 m for impurities accumulation in the bottom of the storage tank.

For sizing the tanks' roofs, it was selected the conic fixed roof type. The stored products have a vapour pressure lower than 0.103 bar, so it was not necessary to have a floating roofs.

The roofs' height was determined by the tangent of 80° (1.40 rad) and the tank diameter.

$$H_{roof} = \frac{D}{2\tan 1.40}$$
(5.17)

The storage tank design results are shown in the table 5.12.

Storage Tank	ST-101	ST-102	ST-103
F _v (m ³ /h)	0.13	0.17	0.04
V _{os} (+20%) (m ³)	109	151	35
P _v (bar) (x 10 ⁻⁶)	5.02	0.06	0.00086
D (m)	7.46	8.30	2.45
H (m)	2.79	3.07	7.65
H _{roof} (m)	0.66	0.73	0.22

Table 5.12: Storage tanks design results.

5.5.2 Equalization and Reflux Tanks

An equalization tank (ET-101) was considered between the wiped film evaporator and the short path distillator, to receive the bulk quantity of by-product B and C in order to perform the change of pressure to 3 mmHg, through the vacuum system installed.

The equipment was sized considering a horizontal tank with elliptical heads and a ratio between the length and diameter of 3. [32, pg. 458] It was considered a residence time of 20 minutes and the design was performed for a tank half-full.

The volume of liquid was determined by the product between the volumetric flow and the residence time considered.

The elliptical head volume, V₀ was obtain from the following equation [35, pg. 627]:

$$V_0 = 0.0778D^3 \tag{5.18}$$

The liquid volume in the heads and cylinder was calculated using the equations shown bellow [35, pg. 627]:

$$V_{heads} = 2V_0 (\frac{H}{D})^2 (1.5 - \frac{H}{D})$$
(5.19)

$$V_{cylinder} = \frac{\pi}{4} D^2 L \frac{1}{2\pi} (\theta - \sin \theta)$$
(5.20)

For a tank half-full, H/D has the value of 0.5 and and the θ angle is 180°. The diameter was obtained using the Microsoft Excel[®] solver tool, by minimizing the difference between the volume of liquid and the sum of the cylinder and heads volume.

For each distillation column, vertical reflux tanks (RD-101 and RD-102) were designed, in order to provide a regular reflux to the column in order to have a normal operation.

The design was performed using the same procedure described above for the equalization tank. It also considered half full tanks and a residence time of 5 minutes.

The equalization and reflux tanks design results are shown in the table 5.13.

Tank	ET-101	RD-101	RD-102	
F _v (m ³ /h)	0.24	0.10	0.23	
V _{liquid} (m ³)	0.081	0.008	0.020	
V _{tank} (m ³)	0.161	0.016	0.039	
V _{heads} (m ³)	0.005	0.001	0.001	
V _{cylinder} (m ³)	0.156	0.016	0.038	
D (m)	0.51	0.24	0.32	
L (m)	1.53	0.71	0.95	

Table 5.13: Equalization and reflux tanks design results.

5.6 Pumps

Pumps were sized for transporting the process liquid fluids. Firstly, it was necessary to perform a piping selection, from the volumetric flows and typical pipe velocity, that ranges between 1 to 3 m/s. [29, pg. 217]

Standard pipe diameters were used to determine the pressure drop per km in the pipe. These values were obtained from a graphical reading in an abacus [36], using the volumetric flow and kinematic viscosity of the pumping streams. To determine the pressure drop in line, fixed values were used for distance estimation and then multiplied by the pressure drop read in abacus:

- Distance between equipments: 0.5 m;
- Distance between process area and storage tanks: 10 m;

The pressure drop in accessories was calculated as 20% of the pressure drop in line. The pressure drop in height was given by the difference between the pump suction and discharge points, making the necessary conversion to pressure units using the fluid density. Some considerations regarding the height estimation are listed bellow:

- All the pumps are in the floor, which is considered as 0 m of height;
- The heights were estimated taking into account the equipments height;
- A standard height of 3.5 m was considered for the storage tanks;
- It was necessary to raise some equipment for NPSH validation: extra height from 2 to 2.5 m;

The total pressure drop is given by the sum of pressure drops in line, accessories and height (see table A.6). To determine the pumps head, it was applied a simplified version of the Bernoulli equation, neglecting the velocity terms:

$$\frac{P_1}{\rho g} + \Delta H_{pump} = \frac{P_2}{\rho g} + \Delta P_{total}$$
(5.21)

The pumps were selected by using a product selection platform in a manufacturer website [37]. It was necessary to insert the volumetric flow, calculated pump head, density and viscosity of the fluid for each pump. The pump sizing tool gives as output the pump head, pump efficiency, capacity and HPSH_{required}. These outputs came with a pump characteristic curve. An example of it can be seen in the figure A.10.

The values inserted in the pump sizing tool and the output results are presented in the tables 5.14 and 5.15.

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109
F _v (m ³ /h)	0.46	0.29	0.20	0.29	0.30	0.20	0.29	0.22	0.20
ΔH_{pump} (m)	33.1	5.6	4.0	5.4	23.7	25.7	4.0	27.2	53.8
ρ (kg/m³)	790	653	746	663	738	834	663	731	535
ν (cSt)	36.0	1.0	1.8	1.0	1.1	3.9	1.0	1.8	14.0

Table 5.14: Pumps input in the manufacturer pump sizing tool.

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109
ΔH_{pump} (m)	36.4	11.8	11.8	11.8	23.9	29.6	11.6	30.4	57.7
η (%)	15.5	24.8	16.9	25.1	17.9	12.1	27.6	14	9.7
Capacity (m ³ /h)	0.48	0.42	0.34	0.43	0.30	0.21	0.50	0.23	0.21
NPSH _{required} (m)	0.74	1.65	1.97	1.66	1.77	1.93	1.74	1.85	2.14

Table 5.15: Output results from the manufacturer pump sizing tool.

For some pumps, it was necessary to insert minimum values, for the volumetric flow and viscosity, tolerated by the manufacturer pump sizing tool, since the real ones were too low (see table A.5). These values are 0.2 m³/h and 1 cSt. An example where it was necessary to use this minimum values is the pump P-103 (volumetric flow) and P-107 (viscosity).

The net positive suction head available (NPSH_{available}) was calculated for each pump, considering that it must be checked if the NPSH_{available} is greater that the NPSH_{required} by the manufacturer, to ensure that cavitation problems will not happen.

NPSH_{available} can be determined by the following equation:

$$NPSH_{available} = \frac{P_1}{\rho g} + z_1 - \frac{P_v(T^\circ C)}{\rho g} - \Delta P_{total}$$
(5.22)

This calculation is referred to the suction section of the pump and the mixture vapour pressure was obtained at suction temperature, multiplying the component mass fraction by their vapour pressure.

The values for the net positive suction head available are presented in the table 5.16. These results include extra height for the cases where it was needed to raise the equipment, ensuring that these values are always greater than the ones shown in the table 5.15.

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109	ſ
NPSH _{available} (m)	0.95	2.26	6.27	2.64	7.36	3.98	2.58	2.86	2.36	ſ

Table 5.16:	Calculated	net positive	suction	head -	NPSH _{available}
-------------	------------	--------------	---------	--------	---------------------------

Centrifugal pumps were chosen as pump type, since the pump selection depends of the volumetric flow and it was the output type from the manufacturer pump sizing tool.

Using the efficiency and pump head values from the table 5.15, the operating power consumption was calculated by the following equation:

$$Power = \frac{\rho g \Delta H_{pump} F_v}{\eta}$$
(5.23)

The operating power consumption results are presented in the table 5.17. These values were used for the calculation of the electricity consumption for the OPEX estimation.

Table 5.17: Pumps operating power consumption.

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109
Power (kW)	0.23	0.03	0.03	0.03	0.08	0.11	0.02	0.10	0.17

5.7 Vacuum Systems

The separation process is entirely performed under vacuum condition. For this reason, it was necessary to design and selected a sequence of vacuum equipment based on their capacities and operating ranges.

The design of a vacuum system must be made in parallel with an economic evaluation, in order to conclude that the final result is the most appropriate. Therefore, it should be noted that the most suitable and economic alternative for a vacuum system arrangement is not the present solution.

To simplify, the vacuum systems were designed as a sequence of ejectors, which are a versatile and inexpensive vacuum pumps type.

Four ejectors sequences (VP-101 to 104) were designed according to the required vacuum in the system. The figure A.11 (see appendix A.5) was used to select the number of ejector stages needed for each vacuum level. For VP-101, VP-102, VP-103 it was selected a sequence with 3 ejectors, while for the VP-104 it was needed a serie of 5 ejectors.

A certain number of preliminary calculations are necessary to determine the required steam to induce the ejector system, evacuating the associated equipment. Thus, the total aspirated flow was calculated, given by the sum of the air leaks and aspirated condensables flows.

To determine the air leaks, it was necessary to estimate the system volume for each ejector series. Some assumptions were made concerning this calculation:

- The system volume just includes the main equipment. For instance, pipes were not considered;
- Volume of the evaporation equipment determined for a cylinder, considering a L/D=3;
- Volume of condensers determined by using the tubes length and bundle diameter;
- Air solubility was considered negligible;

The air leaks were determined using the figure A.12, by inserting the system estimated volume and pressure. For design purposes it is considered twice the value of air leaks obtained. [38, pg. 366]

The aspirated condensables were calculated by using the following equation. Only the majority compounds were considered for the vapour pressures calculation (see table 5.18).

Aspirated Condensables =
$$\frac{P_v \frac{airleaks}{M_{air}}}{P_{system} - P_v}$$
(5.24)

In the table 5.18 are shown the values related with the estimation of the total aspirated flow for each vacuum system.

The required steam to induce each ejector system was determined using the figure A.13 shown in the appendix A.5.

To select the adequate curve to read the values, the percentage of air in the total aspirated flow was calculated. The curve selection was made in the following way:

• Curve "three stage, barometric intercondensers (5) - 100% air mixture" for VP-101 and VP-102;

Ejector System	VP-101	VP-102	VP-103	VP-104
P _{system} (mmHg)	5	3	2.5	0.15
V _{equipment} (m ³)	2.56	0.16	2.31	0.02
Air leaks (kg/h)	1.81	0.23	0.86	0.09
P _v (mmHg)	3.51	1.56	2.49	0.12
Aspirated Condensables (kg/h)	0.148	0.009	8.325	0.012
Total aspirated (kg/h)	1.965	0.235	9.187	0.102

Table 5.18: Estimation of the total aspirated flows.

- Curve "three stage, barometric intercondensers (5) 10% air mixture" for VP-103;
- Curve "five stage, c (6)" 100% for VP-104;

This curve was constructed based on mixtures of air and water vapour, so it was necessary to correct the obtained values for air equivalent quantities, since the mixture aspirated comprises other vapours. To perform this correction, the definition of entrainment ratio was used :

$$Entrainment \ Ratio = \frac{weight \ of \ gas}{weight \ of \ air}$$
(5.25)

In the expression above, the weight of air corresponds to the air equivalent. The entrainment ratio was obtained from the figure A.14 by inserting the average molecular weight for each vacuum system. Applying these values to the equation above, an air equivalent value at 70° F for each ejector series was obtained.

Then, it was necessary to correct the air equivalent value to the temperature of the aspirated vapours, using another value of entrainment ratio, obtained for each temperature by the curve A.15. The values were read in the steam curve. The air equivalent value was then applied to the required steam value.

The required steam flow to induce each ejector are shown in the table 5.19.

Table 5.19: Required steam flow for each ejector system.

Ejector System	VP-101	VP-102	VP-103	VP-104
Required Steam (kg/h)	22.13	4.49	111.39	4.84

Chapter 6

Cost Estimation Model

To estimate the costs associated to the design, construction and operation of the project, a preliminary cost estimation model was implemented with an accuracy of +/- 50%. Using this cost model, both capital expenditure (CAPEX), comprising the cost of fixed assets and further improvements, and operational expenditure (OPEX), which include the ongoing costs for the project, were obtained.

Total costs associated to a possible extension of the existing Amyris-Total EN project, accounting with the valorization of by-products, were determined from CAPEX and OPEX estimation. A final evaluation of by-products valorization opportunity was also performed by comparison of calculated by-products feed and farnesane D (grade Diesel) prices.

This chapter is presented in a confidential appendix.

Chapter 7

Conclusions

7.1 Conclusions

The main objective of the present work was a separation process development and a preliminary cost estimation, in order to consider the valorization of the distillation bottom from the existing Amyris-Total farnesane production process.

A by-products separation process was developed based in a laboratory separation, through process model simulation in Aspen Plus v7.3.

A base case model was performed using a bottoms feed composition after farnesane recovery and a feed flow of 300 kg/h. The separation scheme used had the following steps: separation between lighter and heavier components, separation between by-products B and C and finally the separation of the remaining farnesane and by-product A.

Representative compounds were selected from the Aspen Plus Database for by-products B and C, since only farnesane and by-product A existed there. In this way, it was possible to obtain a proper estimation of properties and vapour-liquid equilibrium, by using the UNIFAC and MXBONNEL Aspen Property Methods.

Wiped film evaporators and short path distillators were used in the separation process development. The separation was performed under vacuum conditions and this type of equipment was used in order to decrease load thermal damage. These equipments were modelled by separation of equipment functions in different Aspen blocks. The wiped film evaporator was modelled using an HEATER to heat transfer process and a FLASH2 for phase separation. For short path distillator, HEATER blocks were used for heat up the load and for the internal condenser then, a SEP2 shortcut block in which the phase separation was performed by defined split fractions.

The by-products separation process development was performed by using a "zero waste" approach, in order to obtain a continuous and efficient process with a minimum of product losses for the study of by-products valorization hypothesis. During the modelling process, it was possible to save an wiped-film evaporator by using a partial condenser after the first rectification column where lighter and heavier compounds were separated.

By-products B and A were the main target by-products, concerning the applicative scenario, due to the characteristics searched by the target-markets. For this reason, it was given priority to the outlet quality for these by-products, namely to a by-product A purity between 92 and 95% and a by-product B flash point greater than 200° C, preferably 210° C. Another requirement was a recovered farnesane within the specification for bio-jet (98.88%).

On the base case model simulation, high by-products recoveries were obtained (values between 93.2 and 99.0%). A lower recovery was obtained for farnesane (78.1%) probably due to solubility with by-product A, because of their similar structure and chemical function. By-product A purity of 90.3% was obtained. This value is lower than the required value mentioned above due to the referred solubility problem. However, target purity could be probably reached if the volatiles stream from the section B.2 was not recovered. By-product B flash point of 209.3° C was reached, which is between the expected range.

A case study model was also performed with the objective of applying the same separation strategy to the bottom stream coming from an existing Aspen simulation of the farnesane K distillation column. The feed composition was more abundant in farnesane than the one used in the base case, so it was necessary to add a distillation column to recover it, assuming for this step a recovery of 95% with a purity within the specifications for bio-jet.

The case study model simulation was performed by comparison with base case recoveries in each separation step. Due to the composition differences, some operational parameters were changed in order to reach the same by-products quality.

Similar results were obtained concerning the by-products total recovery (values between 92.9% and 98.9%). However, by-product A purity and by-product B flash point values were lower than the base case (85% and 206.7° C, respectively).

A cost estimation model was developed based in the simplified equipment design performed from the base case model simulation results, including CAPEX and OPEX estimations. It was considered a linear amortization over a period of 15 years for CAPEX annualization and an operational period of 8200 h/year for OPEX annualization. The project would be installed in France.

About 60% of the CAPEX breakdown corresponds to direct costs. So, from the direct cost distribution, shares of 61 and 15% were verified for evaporation equipment and pumps, respectively. These results can be explained by the provision values used for the estimation of the unknown equipment cost (wiped film evaporator and short path distillator), including the selection of API pumps type, which are quite expensive.

Regarding the OPEX results, it was concluded that fixed production costs are more important than the variable production costs, accounting with 74% and 26% of share, respectively. In the variable cost distribution, steam accounts with a share of 77% used for the vacuum system followed by the natural gas with 15% for the heating oils running system. A share of 96.5% corresponds to labour costs in the fixed production costs.

There is a valorization opportunity for the by-products, since the obtained by-products bottoms' prices (A - 0.81 USD/L and B - 1.14 USD/L), for both by-products prices possibilities, were greater than farne-

60

sane D price (0.50 USD/L), which means that a by-products separation process may be implemented.

7.2 Future Work

Regarding a possible future work concerning the obtained results some suggestions are left:

- An optimization of the separation model between by-products B and C can be performed, by using more rigorous Aspen modelization (replace the SEP2 block in which the separation was performed by defined split fractions);
- An equipment design and cost estimation model can also be developed based in the case study model simulation results;
- Since there is valorization opportunity, specialized manufacturers must be consulted in order to verify and complete the equipment design results and separation process scheme;
- Based in the manufacturers' quotations, a cost estimation model with a higher accuracy can be performed in order to verify the first value obtained in this work.

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Bibliography

- [1] Korneel Rabaey and Arthur J Ragauskas. "Editorial Overview: Energy Biotechnology". *Current opinion in biotechnology*, 27:1–2, 2014.
- [2] International Energy Agency. "Renewables Energy Outlook: World Energy Outlook". Annual Report, 2013.
- [3] Peter McKendry. "Energy production from biomass (part 1): overview of biomass". *Bioresource technology*, 83(1):37–46, 2002.
- [4] EUROPEAN PARLIAMENT. "DIRECTIVE 2009/28/EC OF THE EUROPEAN PARLIA-MENT:Promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC". 2009.
- [5] Charlène Sagnes and Marie-Françoise Chabrelie. "Biocarburants de deuxième génération: une nouvelle étape est franchie", January 2015. IFPEN.
- [6] Sang Yup Lee, Hye Mi Kim, and Seungwoo Cheon. "Metabolic engineering for the production of hydrocarbon fuels". *Current opinion in biotechnology*, 33:15–22, 2015.
- [7] TOTAL. "TOTAL in brief". Brochure, 2014.
- [8] TOTAL. "Biomass meeting the biotechnological challenge". Brochure, 2014.
- [9] Luis Caspeta, Nicolaas AA Buijs, and Jens Nielsen. "The role of biofuels in the future energy supply". *Energy & Environmental Science*, 6(4):1077–1082, 2013.
- [10] Man Kee Lam and Keat Teong Lee. "Microalgae biofuels: a critical review of issues, problems and the way forward". *Biotechnology advances*, 30(3):673–690, 2012.
- [11] EPA Combined Heat and Power Partnership. "The Biomass CHP Catalog of Technologies". technical publication, 2007.
- [12] Khanok Ratanakhanokchai, Rattiya Waeonukul, Patthra Pason, C Aachaapaikoon, Khin Lay Kyu, Kazuo Sakka, Akihiko Kosugi, and Yutaka Mori. "Paenibacillus curdlanolyticus strain B-6 multienzyme complex: A novel system for biomass utilization". *Biomass Now-Cultivation and Utilization*, 2013.

- [13] Yining Zeng, Shuai Zhao, Shihui Yang, and Shi-You Ding. "Lignin plays a negative role in the biochemical process for producing lignocellulosic biofuels". *Current opinion in biotechnology*, 27: 38–45, 2014.
- [14] Frank Behrendt, York Neubauer, Michael Oevermann, Birgit Wilmes, and Nico Zobel. "Direct liquefaction of biomass". *Chemical engineering & technology*, 31(5):667–677, 2008.
- [15] AV Bridgwater. "Renewable fuels and chemicals by thermal processing of biomass". Chemical Engineering Journal, 91(2):87–102, 2003.
- [16] JJC Geerlings, JH Wilson, GJ Kramer, HPCE Kuipers, A Hoek, and HM Huisman. "Fischer–Tropsch technology:from active site to commercial process". *Applied Catalysis A: General*, 186(1):27–40, 1999.
- [17] ATAG. "Facts & Figures". http://www.atag.org/facts-and-figures.html. Accessed: 21-10-2015.
- [18] F Rosillo Calle, D Trhan, M Seiffert, and S Teeluckingh. "The potential and role of biofuels in commercial air transport-biojetfuels - Task 40: Sustainable Intenational Bioenergy Trade.". https://www.dbfz.de/fileadmin/user_upload/Referenzen/Statements/IEA_ T40_Biojetfuel.pdf, 2012.
- [19] Bryan R Moser. "Camelina (Camelina sativa L.) oil as a biofuels feedstock: Golden opportunity or false hope?". *Lipid technology*, 22(12):270–273, 2010.
- [20] Zainul Abideen, Raziuddin Ansari, Bilquees Gul, and M Ajmal Khan. "The place of halophytes in Pakistan's biofuel industry". *Biofuels*, 3(2):211–220, 2012.
- [21] UOP Honeywell. "Honeywell Green Jet Fuel". http://www.uop.com/processing-solutions/ renewables/green-jet-fuel/. Accessed: 22-10-2015.
- [22] TOTAL. "Designing Innovative Bio-Products Together: Bio-Components Day". PowerPoint presentation, 2014.
- [23] Noah I Tracy, Daichuan Chen, Daniel W Crunkleton, and Geoffrey L Price. "Hydrogenated monoterpenes as diesel fuel additives". *Fuel*, 88(11):2238–2240, 2009.
- [24] EPA. "Food and Agricultural Industry Sugar Cane Processing". http://www.epa.gov/ttn/chief/ ap42/ch09/final/c9s10-1a.pdf. Accessed: 07-06-2015.
- [25] UIC GmbH. "Thin Film Evaporator and Short Path Distillators". Technical Documentation.
- [26] Melvin A Durán, Rubens Maciel Filho, and Maria R Wolf Maciel. "Rate-based modeling approach and simulation for molecular distillation of green coffee oil". *Computer Aided Chemical Engineering*, 28:259–264, 2010.
- [27] Aspen Technology. "Aspen Physical Property System: Physical Property Methods", 2010.

- [28] Nongluk Chawankul, Supaporn Chuaprasert, Peter Douglas, and Wilai Luewisutthichat. "Simulation of an agitated thin film evaporator for concentrating orange juice using AspenPlus TM". *Journal of food engineering*, 47(4):247–253, 2001.
- [29] RK Sinnott. "Coulson & Richardson's Chemical Engineering", volume 6. 3rd edition, 1999.
- [30] Gavin Towler and Ray K Sinnott. "Chemical Engineering Design: principles, practice and economics of plant and process design". Elsevier, 2012.
- [31] "Fuel gases: Heating values". http://www.engineeringtoolbox.com/ heating-values-fuel-gases-d_823.html. Accessed: 13-08-2015.
- [32] Carl Branan. "Rules of Thumb for Chemical Engineers". 3th edition, 2005.
- [33] WY Svrcek and WIJ Monnery. "Design Two-Phase Separators Within". Chemical engineering progress, pages 53–60, 1993.
- [34] John J. McKetta Jr. "Encyclopedia of Chemical Processing and Design", volume 65. CRC Press, 1998.
- [35] Stanley M. Walas. "Chemical Process Equipment Selection and Design". Butterworth-Heinemann, 1990.
- [36] Association Français de Techniciens du Pétrole. "Abaques de Paul Lefèvre pour le calcul des pertes de charge des liquides dans le conduites". 7^e edition, 1981.
- [37] Grundfos. "Grundfos Product Center Sizing Tool". http://product-selection.grundfos.com/ sizing-by-application.html. Accessed: 29-07-2015.
- [38] Ernest E. Ludwig. "Applied Process Design For Chemical and Petrochemical Plants", volume 1.
 Butterworth-Heinemann, 3th edition, 1999.
- [39] Shell Lubricants. "Technical data sheet: Shell Heat Transfer Oil S2". http://s02.static-shell. com/content/dam/shell/static/ind/downloads/lubes-b2b/other-shell-lubricants/ heat-transfer-oil.pdf, 2010. Accessed: 15-07-2015.
- [40] Sulzer. "Structured Packings". http://www.sulzer.com/da/-/media/Documents/ ProductsAndServices/Separation_Technology/Structured_Packings/Brochures/ Structured_Packings.pdf. Accessed: 16-07-2015.
- [41] Ernest E. Ludwig. "Applied Process Design For Chemical and Petrochemical Plants", volume 3.
 Butterworth-Heinemann, 3th edition, 1999.
- [42] Don W. Green and Robert H. Perry. "Perry's Chemical Engineers' Handbook". McGraw-Hill, 8th edition.

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Appendix A

Equipment Design

A.1 Evaporation Equipments

er mal Conductivity

Prandtl No.

Typical Design Data	1				
Temperature	°C	0	20	40	100
Density	kg/m3	876	863	850	811
Specific Heat Capacity	kJ/kg*K	1.809	1.882	1.954	2.173

0.136

3375

W/m*K

Figure A.1: Ty	pical design data -	Commercial I	heating oil (Shell Heat	Transfer O	il S2).	[39]

0.133

375

0.128

69

0.134

919

200

746

2.538

0.121

20

150

778

2.355

0.125

32

250

713

2.72

0.118

14

300

68

2.902

0.114

11

340

655

3.048

0.111

9



Figure 12.1. Overall coefficients (join process side duty to service side and read U from centre scale)

Figure A.2: Estimation of the overall heat transfer coefficient for evaporation equipment. [29, pg. 369]

A.2 Distillation Columns



Figure A.3: Auxiliary curves for the packed distillation column design - Mellapak 250Y. [40, pg. 6]

A.3 Heat Transfer Equipment

Cold utility	Cooling water	Chilled water		
ρ (kg/m³)	995.67	999.53		
μ (N s/m²)	0.00083	0.00123		
Cp (kJ/kg K)	4.173	4.184		
k (W/m K)	1.413	1.470		

Table A.1: Cold utilities average physical properties - cooling water and chilled water (P=1.5 bar).

Table A.2: Standard tubing characteristics	 Adapted from 	[41, pg.	22]
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d _o (mm)	Thickness (mm)						
6.35	0.71	0.56	0.46	0.41			
9.53	1.24	0.89	0.71	0.56			
12.7	1.65	1.24	0.89	0.71			

Table A.3: Standard tube length. [29, pg. 645]

Length (m)	0.61	1.22	1.83	2.44	3.66	4.88	6.10	7.32
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Figure A.4: Shell-bundle relation for determine shell diameter. [29, pg. 647]

Square pitch, $p_t = 1.25d_o$									
No. passes	1	2	4	6	8				
<u>K</u> 1	0.215	0.156	0.158	0.0402	0.0331				
n_1	2.207	2.291	2.263	2.617	2.643				

Figure A.5: Constants used for determine bundle diameters. [29, pg. 649]



Figure A.6: Shell side friction factors. [29, pg. 673]



Figure A.7: Tube side friction factors. [29, pg. 667]



Figure A.8: Average vapour flow rate factor - pressure drop for partial condensers. [29, pg. 721]

Correction factor method - plate heat exchangers

For plate heat exchangers, the correction factor F is related with the number of transfer units - NTU and the flow arrangement (figure A.9). The flow arrangement used was 1:1 and NTU was calculated by the following equation. For rough sizing purposes the factor F can be 0.95. [29, 756-757]

$$NTU = \frac{(T_o - T_i)}{\Delta T_{LM}} \tag{A.1}$$



Figure A.9: Correction factor for plate heat exchangers. [29, pg. 757]

In the table A.4 are shown the NTU and factor F values for the plate heat exchangers.

Heat Exchanger	E-103	E-104	E-105	E-106
NTU	1.8	2.0	2.2	2.4
F	0.96	0.96	0.95	0.95

Table A.4: NTU and correction factor F - plate heat exchanger.

A.4 Pumps



Figure A.10: Example of a pump characteristic curve output, from manufacturer sizing tool - P-101. [37]

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109
Q _v (m ³ /h)	0.46	0.29	0.13	0.29	0.30	0.16	0.28	0.22	0.05
ν (cSt)	35.94	0.32	1.80	0.27	1.05	3.89	0.29	1.76	14.48
ρ (kg/m³)	790	653	746	663	737	834	663	731	535

Table A.5: Preliminary data for pump design.

Pumps	P-101	P-102	P-103	P-104	P-105	P-106	P-107	P-108	P-109
Real pipe D (mm)	9.24	8	5	8	8	6	8	6.833	5
Pressure Drop (bar/km)	210	35	140	35	40	70	35	60	140
Distance (m)	10	0.5	0.5	0.5	10	10	0.5	10	10
Pressure Drop in line (bar)	2.1	0.018	0.07	0.018	0.4	0.7	0.018	0.6	1.4
Pressure Drop in acessories (bar)	0.42	0.004	0.014	0.004	0.08	0.14	0.004	0.12	0.28
Z ₂ - Z ₁	1.25	5.3	0.5	5.13	3.5	3.5	3.15	3.5	3.5
Pressure Drop in height (bar)	0.099	0.346	0.037	0.340	0.258	0.291	0.209	0.256	0.187
Total Pressure Drop (bar)	2.619	0.367	0.121	0.361	0.737	1.131	0.230	0.976	1.867

Table A.6: Total pressure drop calculation.

A.5 Vacuum Systems



Figure A.11: Vacuum levels reached with the several equipment types. [42, pg. 10-60]



Figure A.12: Air leakage estimation in ejector systems. [38, pg. 367]



Figure A.13: Steam required for a ejector system. [38, pg. 372]



Figure A.14: Molecular weight entrainment ratio curve. [38, pg. 361]



Figure A.15: Temperature entrainment ratio curve. [38, pg. 360]