UNIVERSITAT ROVIRA i VIRGILI

PROCESS DEVELOPMENT STUDY OF THE PRIMARY SEPARATION UNIT FOR A SYNGAS CONVERSION PROCESS

Master thesis presented by David Raya Rodríguez
to obtain the master's degree in Chemical Engineering
from the *Universitat Rovira i Virgili*

Company Supervisor: Alistair Hughes

URV Tutor: Armand Llauradó

Tarragona, 9 June 2023

[This page intentionally left blank]

Table of contents

NOMENCLATURE

ASME	American Society of Mechanical Engineers
CAPEX	Capital expense
C_i	Hydrocarbons with *i* carbon atoms
C_i+	Hydrocarbons with more than *i* carbon atoms
DME	Dimethyl ether
DMPEG	Dimethyl ethers of polyethylene glycol
FTM	Facilitated transport membrane
H/h	Enthalpy
HAZOP	Hazard and operability study
IPCC	Intergovernmental Panel on Climate Change
IRR	Internal rate of return
JT	Joule-Thompson
KPI	Key performance indicators
LTHV	Long term hydrocarbon values
MOF	Metal–organic frameworks
MRF	Materials recovery facility
MSW	Municipal solid waste
NGL	Natural gas liquates
NPV	Net profit value
NRTL	Non-random two liquids (thermodynamic model)
Ø	Diameter
OPEX	Operational expense
P&ID	Process and instrumentation diagram
P/p	Pressure
PENG-ROB	Peng-Robinson (thermodynamic model)
P_H	High pressure
P_I	Intermediate pressure
P_L	Low pressure
PSA	Pressure swing adsorption
PSRK	Predictive Soave-Redlich-Kwong (thermodynamic model)

PTSA	Pressure and temperature swing adsorption
Q	Volumetric flow
R&D	Research and development
RK	Redlich-Kwong (thermodynamic model)
RSV	Recycle split vapor
SRK	Soave-Redlich-Kwong (thermodynamic model)
T	Temperature
TEA	Triethanolamine
TEG	Triethylene glycol
TRL	Technology readiness level
TSA	Temperature swing adsorption
UNIFAC	UNIQUAC functional group activity coefficients (thermodynamic model)
UNIQUAC	Universal quasichemical (thermodynamic model)
V	Volume
VOC	Volatile organic compounds
VPSA	Vacuum pressure swing adsorption
Z	Length
m_i	Mass fraction of the molecule i in the liquid phase
x_i	Molar fraction of the molecule i in the liquid phase
y_i	Molar fraction of the molecule i in the vapor phase
μ	Dynamic viscosity
ρ	Density
Φ	Bed porosity

The following units are defined throughout the report as:

ppmv	$x_i \cdot 10^6$
ppmm	$m_i \cdot 10^6$

The word *Aspen* throughout the report is referred to the software *Aspen Plus V11*.

The word *Dow* throughout the report is referred to the corporation *The Dow Chemical Company* (*Dow Inc.*).

LIST OF FIGURES AND TABLES

List of figures of the project (appendices excluded)

List of figures of the project (appendices excluded) (cont.)

List of figures of the project (appendices excluded) (cont.)

List of tables of the project (appendices excluded)

SUMMARY

As a response to climate change, companies are developing and implementing diverse strategies to reduce greenhouse gas emissions. To this end, circular economy is a widely-adopted approach, as it focuses on regenerating materials and products. This strategy is already present in the plastics industry, where polymers are recycled to produce new feedstock. Chemical recycling is one of the research cornerstones in the polymers industry, with gasification emerging as a promising technique. This process transforms plastic waste into syngas that can subsequently be transformed into hydrocarbons.

In this regard, Dow is assessing the viability of various syngas conversion technologies, which involves the use of an innovative hybrid catalyst to obtain hydrocarbons from syngas. Within this context, the goal of this project is to determine the best separation strategy for recovering hydrocarbons from the outlet mixture of the syngas reactor.

To accomplish this, an extensive literature research was conducted to identify commercially-available or under-development technologies capable of performing the separation. The recovery of water, carbon dioxide and hydrocarbons was assessed using a combination of heuristics, simulation software and Dow's internal methodologies.

After a careful evaluation of water removal technologies, molecular sieves were selected as the most suitable method for separating water. Molecular sieving demonstrated exceptional recovery and selectivity capabilities, achieving low concentrations of water in the treated gas with minimal energy consumption. Conversely, glycol absorption could only achieve comparable specifications at the cost of a lower selectivity and higher energy requirements.

Carbon dioxide recovery technologies were also evaluated, with amine washing identified as the best strategy. Amine washing could achieve sub-ppm concentrations of carbon dioxide in the treated stream while still offering high selectivity and relatively low energy consumption. On the other hand, physical absorption technologies required significant refrigeration when aiming low concentrations of carbon dioxide in the treated gas, resulting in elevated energy consumptions. Additionally, a significant fraction of hydrocarbons was lost in the absorption column when using physical absorption technologies.

For hydrocarbon recovery, cryogenic and extractive distillation methods were assessed. (i) Regarding cryogenic distillation and to achieve the low temperatures required, the installation of either an N_2-CH_4 refrigeration cycle or a turbo-expander was necessary to complement existing refrigeration cycles. Turbo-expansion was selected over mixed refrigerant systems to avoid the installation of additional facilities in the plant. Further analyses were conducted to compare the present work with alternative chemistries and previous work. (ii) Regarding extractive distillation, the use of pentane as an entrainer was selected over other solvents for its lower energy consumption. A best-case scenario was identified through different sensitivity analyses. (iii) Cryogenic distillation was chosen over extractive distillation due to its lower energy consumption.

Consequently, the proposed separation train for the recovery of hydrocarbons from the outlet mixture of the reactor consists of three steps: amine washing to recover carbon dioxide, molecular sieving to remove water and cryogenic distillation with turbo-expansion to recover hydrocarbons.

1 INTRODUCTION

1.1 Background

The warming of the climate system is unequivocal. Many natural systems are being affected by regional climate changes in the form of higher temperatures, rise of the sea level, increased or decreased precipitations, etc. The IPCC (2007) states that the global average temperature increment since the mid-20th century is very likely caused by the increase of the concentration of anthropogenic greenhouse gases such as CO_2, methane, and nitrous oxide. If emissions remain at current rates or increase, effects of the global climate warming would very likely be larger than those observed during the last century.

Societies can respond to climate change by adapting to its impacts (reducing the vulnerability, both in the short and the long term) and by reducing greenhouse gas emissions (mitigating climate change). There is high confidence that neither adaptation nor mitigation alone can avoid all climate change impacts, but they can complement each other to significantly reduce its risks (IPCC, 2007).

It is in this context that circular economy arises. This economic system is based on reducing and regenerating materials and products; and emphasizes on achieving a carbon-neutral society by reducing feedstock consumption, increasing resource efficiency at all levels of the value chain, and extending the lifespan of products (IPCC, 2007; Mohan & Katakojwala, 2021).

For the case of the chemical industry, drivers that build up circularity have been suggested by various authors in the literature. Some of the drivers proposed by Mohan & Katakojwala (2021) are: closing loops, utilizing renewable raw materials, achieving net zero emissions, using new chemistry and innovative technologies, and cooperating for industrial symbiosis.

The Dow Chemical Company (henceforth *Dow*) is actively working on these drivers to approach a circular petrochemical industry and to achieve CO_2 neutrality in its Terneuzen site by 2050. For this purpose, it is following a Multi Generation Plan (so called "roadmap towards carbon neutrality") that consists of three generations (The Dow Chemical Company, n.d.):

- **Generation 1** (2028): off-gas from the crackers (methane) is converted into hydrogen. Hydrogen produced is reused to fuel the crackers, achieving a carbon-free combustible. Carbon dioxide generated is captured, transported, and stored. With the emissions of 2021 serving as the baseline, a reduction of 35 % of the CO_2 emitted into the atmosphere is aimed.
- **Generation 2** (2030): gas turbines fed with methane are replaced by electrical drivers. Other off-gas-based equipment is also replaced using hydrogen produced on-site. With the emissions of 2021 serving as the baseline, a reduction of 42.5 % of the CO_2 emitted into the atmosphere is aimed.
- **Generation 3** (2050): by powering crackers with renewable electricity, unused hydrogen is used in other processes and is supplied to other industrial partners of the region of the Netherlands and Belgium. With the emissions of 2021 serving as the baseline, a reduction of 95 % of the CO_2 emitted into the atmosphere is aimed.

The advancements made in these generations are going to allow the delivery of innovative circular economy solutions by focusing on circular materials, technologies and value chain ecosystems.

One of the industrial sectors where there is a large focus on circularity is in the plastics industry. The production of polymeric materials is currently being fed by fossil feedstocks. Crude oil is fractionated to obtain, among others, naphtha, that is supplied to steam crackers to produce ethylene and propylene. These hydrocarbons are polymerized to obtain plastics, further processed to manufacture consumer goods. After its usable life, polymeric materials can be recycled into new products or utilities in three different ways: mechanical recycling, chemical recycling and energy recycling (*The Different Types of Recycling*, 2021).

Although both mechanical and chemical recycling can be used to close the loop from a mass balance perspective, products obtained with mechanical recycling can lose quality after being recycled more than once and are eventually degraded. Despite its inherent challenges, chemical recycling has the potential to restore high-quality raw materials, making it a significant focus of research within the polymers industry. Feedstock obtained from revalorized polymeric residues can be complemented with bio-based and fossil feedstock to make-up losses throughout plastics' circular life and to accomplish market needs.

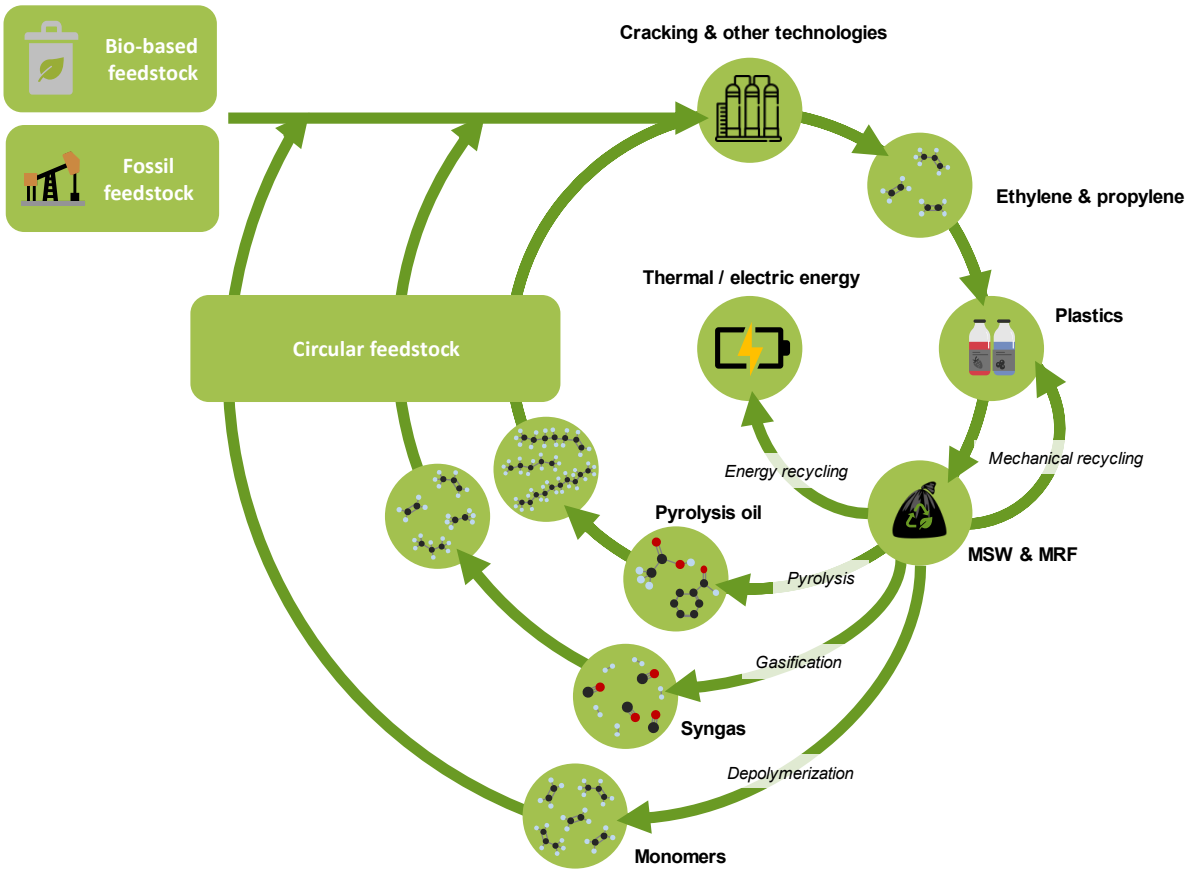

Figure 1.1. Integration of different recycling strategies in the production of polymeric materials. Source of information: The Different Types of Recycling (2021)

1.2 Syngas conversion process

Fischer–Tropsch is one of the technologies used to obtain hydrocarbons from syngas. Although operating conditions and other design parameters are key variables that determine the composition of the syncrude, this reaction has a high yield to heavy paraffinic hydrocarbons (de Klerk, 2013).

An alternative chemical pathway to obtain hydrocarbons from syngas is methanol synthesis. This two-step route (from syngas to methanol and from methanol to hydrocarbons) requires dedicated reactors operating at different conditions. In contrast to Fischer–Tropsch, these reactions have a high yield to light hydrocarbons and a great selectivity to olefins (Nieskens et al., 2017).

Dow is assessing new technologies to combine both steps using a single reactor with a hybrid catalyst, where the methanol synthesis element is coupled to the methanol conversion component.

The methanol synthesis catalyst is typically a mixed metal oxide, described by Nieskens et al. (2017), Santos et al. (2020) and other authors in the literature as copper-zinc, chromium-zinc or zirconium-zinc metal oxides. Dopants such as Fe, Al and Ga are usually added to improve the performance of the catalyst and to maintain high CO conversion and olefin stability over time (Pollefeyt et al., 2022).

The methanol conversion catalyst is typically a molecular sieve/zeolite. Nieskens et al. (2018) affirm that SAPO-34 is a preferred catalyst for the methanol to light olefins processes and is used by Nieskens et al. (2017), Pollefeyt et al. (2022) and Santos et al. (2020) for the direct conversion of syngas to olefins.

Depending on the nature of the catalyst, the reaction is more selective towards olefins or towards paraffins. The choice of hydrocarbon producing technology determines the flowsheet configuration as well as the configuration and energy requirement of the separation units. It can be envisioned that this process would take place using the hybrid catalyst in a reactor, from which a stream with hydrocarbons, unreacted syngas and methane is obtained. After a separation process to recycle syngas to the reactors and to purge methane, the hydrocarbon stream obtained can be utilized by the company to produce other consumer goods.

[This page intentionally left blank]

2 BASIS OF THE PROJECT

2.1 Objectives and scope

The objective of this project is to evaluate the separation strategy for recovering hydrocarbons from the syngas conversion reactor outlet mixture.

The scope of the project encompasses the scouting of different commercially available technologies for the recovery of the different species of the mixture and, for each of the chosen strategies, the simulation of the process and the evaluation of KPI. At the end of the project, a comparison between the strategies is performed and a best-case is provided.

Tasks out of scope for this project are:

- Study of the process downstream of the hydrocarbon's primary separation.
- Simulation of auxiliary streams (e.g., utilities) and the associated equipment.
- Detailed simulation and/or design of equipment and pipelines.
- Viability analysis of the project (cashflows, NPV, IRR).

2.2 Basis of engineering

The main feed of the process is the gas stream that leaves the syngas conversion reactor. The composition of the stream from which hydrocarbons must be recovered is found in Table 2.1 and enters the process at 35 °C and above 20 bara. The design basis for the flowrate was determined by a required fixed production of light olefins from the overall process.

Table 2.1. Typical reactor product composition.

Species	Molar fraction (%)
Hydrogen	65 – 85
Carbon monoxide	4 – 15
Carbon dioxide	2 – 10
Methane	2 – 5
C_2-C_5	3 – 5
Water	Saturation at inlet conditions
Nitrogen	0 – 4

The main outlets of the process are light hydrocarbons (product), recovered syngas, process water, recovered CO_2 (technology dependent), methane (optional) and purged gas. The composition of each of the streams is an object of study for this project.

Criteria or restrictions that must be considered when performing the study are:

- Water concentration after dehydration must be under 1 ppmv.
- Carbon dioxide concentration for cryogenic separation must be below 50 ppmv.
- Carbon monoxide concentration in the product stream determined by product work-up feedstock specifications.
- Methane concentration in the product stream must be under 1000 ppmm.
- Methane purge rate is determined by the methane selectivity of the hybrid catalyst.
- Nitrogen purge rate is determined by the rate at which inert enters the process through gasification or methane reforming using oxygen.
- Recovered syngas must be recycled to a pressure above 20 bara.

3 STUDENT'S ROLE IN THE COMPANY

3.1 The Dow Chemical Company

Dow is an American chemical corporation headquartered in Midland (MI), U.S.A. Its portfolio of plastics, industrial intermediates, coatings and silicones businesses delivers a broad range of differentiated, science-based products and solutions for its customers in high-growth market segments, such as packaging, infrastructure, mobility and consumer applications. The company is positioned among the top three chemical producer firms by sales (Dow Inc., 2022; Tullo, 2022).

With 104 manufacturing sites in 31 countries, it employs more than 35,000 people and delivered net sales of approximately $55 billion in 2021 (Dow Inc., 2022). The distribution of the company manufacturing sites is illustrated in Figure 3.1.

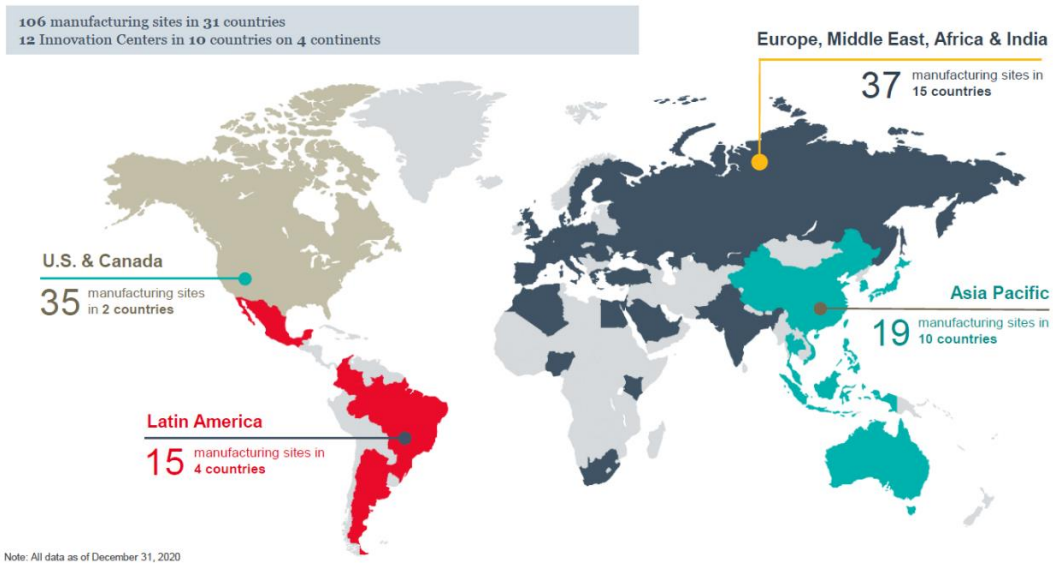

Figure 3.1. Distribution of Dow´s manufacturing sites. Source: Santos & Sabatino (n.d)

Dow's ambition, purpose, goal and values are illustrated in Figure 3.2.

Figure 3.2. Dow's ambition, purpose, goal and values. Source: Dow Inc. (2022)

3.1.1 Community, inclusion, diversity and equity

Dow creates meaningful impact in areas that connect science, people and community across the globe through charitable investments, employee volunteerism and global and local partnerships. An exemplification of this impact is Dow's Business Impact Fund, created to give Dow businesses the resources to develop projects that create market opportunities by solving social problems through the company's technology and expertise (Dow Inc., 2022).

Other examples of how the company addresses world's social challenges are:

- Launch of Employee Relief Fund to support employees affected by Hurricane Ida, Hurricane Nicholas and flooding in India
- Support of mental health programming as needs grew from the pandemic and provision of additional COVID-relief support for Argentina, Brazil, Colombia, India and Mexico.
- Organization of 195 cleanups with approximately 7,500 people taking part in 32 countries, with approximately 390,000 pounds of waste removed from the environment.

Regarding inclusion, diversity and equity, the company committed $13 million as part of Dow ACTs: a framework design to address systematic racism and inequity within the company and in the communities.

In fact, inclusion, diversity and equity are embedded into the corporate strategy, built on seven global foundational pillars that focus on the employees, suppliers, customers and communities. Inclusion, diversity and equity are fostered by people leaders in the company and is a key factor for attracting and developing talent. This inclusive culture is catalyzed through Employee Resource Groups, clubs of employees that represent different dimensions of diversity and are safe havens for employees to see themselves, be themselves and to be heard (Dow Inc., 2022).

3.1.2 Environmental performance

Dow is committed with sustainability and world-class environment, health and safety performance throughout all its history. The company is currently executing on their 2025 Sustainability Goals that set the standard for the chemical industry by focusing on more sustainable ways to do business and leading the transition to a more sustainable future (Dow Inc., 2022).

2025 Sustainability Goals are listed below (Dow Inc., 2022):

- **Leading the blueprint**: to integrate public policy solutions, science and technology, and value chain innovation to develop sustainable societal blueprints.
- **Delivering breakthrough innovations**: to deliver breakthrough sustainable chemistry innovations that advance the well-being of humanity.
- **Advancing a circular economy**: to advance a circular economy by delivering solutions to close the resource loops in key markets.
- **Valuing nature**: to apply business decision processes to complete projects that increase business value and are better for ecosystems.

- **Safe materials for a sustainable planet**: to achieve a future where every material brought to the market is sustainable for people and the planet.
- **Engaging for impact (communities, employees and customers)**: to engage people worldwide to apply their passion and expertise to advance the well-being of people and the planet.
- **World-leading operations performance**: to maintain world-leading operation performance in natural resource efficiency, environment, health and safety.

To accelerate the sustainability agenda, Dow set multi-decade targets to put the company on a path to achieve carbon neutrality and eliminate plastic waste (Dow Inc., 2022):

- **Protect the climate**: by 2030, Dow aims to reduce its net annual carbon emissions by 5 million metric tons compared to its 2020 baseline (15 % reduction). By 2050, Dow intents to be carbon neutral.
- **Stop the waste**: by 2030, Dow will enable 1 million metric tons of plastic to be collected, reused or recycled through its direct actions and partnerships.
- **Close the loop**: by 2035, Dow will enable 100 % of its products sold into packaging applications to be reusable or recyclable.

More information related to the objectives for 2050 can be found in *1.1. Background*.

3.1.3 Dow Benelux & Terneuzen site

Dow Benelux is divided in eight locations: Delfzijl, Dordrecht and Terneuzen in the Netherlands, and Zwijndrecht, Antwerpen, Brussel, Seneffe and Tertre in Belgium. Production sites, R&D innovation centers and service hubs are distributed among all these locations, with a workforce of 4200 employees. This makes Dow Benelux hub the second Dow's biggest hub.

Dow Terneuzen is the biggest among Benelux, with 3550 employees and between 500 and 2000 contractors. The site was established in 1962, and has 440 hectares and 17 plants; producing more than 800 products.

3.2 Role of the student

The internship was carried out in Dow´s Terneuzen site in the R&D department of *Syngas & FCDh*, collaborating to the *Packaging & Specialty Plastics and Hydrocarbons* business.

The role held by the student was of process development engineer. The student was responsible for evaluating the separation strategy for recovering hydrocarbons from a syngas conversion reactor outlet mixture by comparing different commercially available technologies. This was done by executing an upfront technology scouting and by using simulation software for a comprehensive process development evaluation. Criteria such as component recoveries, product purities, energy consumption and CAPEX were evaluated to decide which is the most suitable technology option.

The main tasks performed are listed below:

- Literature research on the most suitable separation strategies. The literature survey covered both commercially available and in development separation technologies. The student had to scout and critically select the information that was relevant for the project and understand how to implement it in process development tasks.
- Process development of the chosen strategies. The student had to sketch out the backbone of the process by tailoring the most fitting technologies found in the literature to the current process.
- Modelling of the chosen strategies from scratch using simulation software or heuristic calculations.
- Comparison of the modelled strategies using techno-economic criteria such as component recoveries, energy consumption, capital costs or operational pragmatism.
- Meetings with professionals working in the project to update them with the status of the project, receive feedback for continuous improvement and share with them the results of the work.

Besides tasks directly related to the project, other assignments and activities were performed to help the student to gain insight into industry, to network with professionals and to develop professional skills. Some of them are:

- Participation in the P&ID reviews and HAZOP analysis of a pilot facility.
- Meetings with professionals from other departments to have a better understanding of the different roles that a chemical engineer can play in the industry.
- Visits to different facilities of the company such as laboratories or pilot and production plants. The objectives are to have a better understanding of the projects carried out in R&D and of the businesses that Dow is participating; and to gain insight of how knowledge acquired during the academical career of the student is translated into reality.
- Participation in company activities organized by Dow or by Employee Resource Groups to expand the student´s network and to explore and enjoy the multicultural environment of the company.

4 LITERATURE RESEARCH OF THE AVAILABLE TECHNOLOGIES

The literature research is focused on determining which are the technologies commercially available or in development for the separation of unreacted feedstock and hydrocarbons from syngas.

Some of the technologies described are industrially established in operations different from syngas processing (e.g., natural gas sweetening), but the similarity between their streams makes them worth analyzing.

4.1 Inert gases recovery

Their non-polarity and their weak physical and chemical interaction with other compounds and materials makes the separation of inert gases from a mixture a challenging operation. For this reason, their removal is practiced by the recovery of the non-inert gas species of the mixture.

4.2 Water removal

As described in Faramawy et al. (2016), removal of water avoids erosion and corrosion of pipelines (especially in presence of carbon dioxide), slug flow caused by water condensation, and formation of hydrates. Water removal is a requirement for cryogenic processing to prevent blockages in the process equipment at low temperatures.

Condensation, membranes, molecular sieves and glycol absorption have been considered for this application. A description of each of these technologies based on the information extracted from literature is found in *Appendix 2*. Table 4.1 (page 22) summarizes and compares the main characteristics of each. The main outcomes of the literature research are detailed hereunder.

Condensation technologies are useful for bulk water removal. Although sub-ppmv concentrations are not achievable, these technologies significantly reduce the humidity level of the stream and decrease the energetic requirements of other equipment. Isenthalpic or isentropic expansions to condense water are useful when large pressure drops are allowed, but as the recycle to the syngas conversion reactor is a large stream that must be re-compressed, expansions are avoided. Refrigeration and compression are expensive and energy-intensive technologies that are not usually used for dehydration because better alternatives are available. However, it is necessary to consider condensation that takes place during the process when making temperature or pressure changes, as the removal of the condensate can lead to a reduction in the energy demand of the selected dehydration unit.

Membrane technologies have been proved capable to recover water from gas streams, but the low partial pressures of water and the high purity of the permeate required make this technology unfeasible. Considering the high pressure ratio between retentate and permeate that is required, only scenarios where large pressure drops are available are feasible.

Despite certain limitations, molecular sieves and glycol absorption units are technologies that can potentially achieve the concentration of water required. Hence, these are the alternatives selected based on the literature pre-screening. These technologies will be modeled and compared in the subsequent sections for further assessment.

Table 4.1. Comparison of water separation technologies.

Criteria	Molecular sieves	Glycol absorption	Condensation	Membranes
State of the technology	Industrial	Industrial	Industrial	Development phase
Applicability to the process	Yes	Yes	Yes	Yes
Recovery of C_2	Very high [1,3] (< 1 ppmv after PTSA)	High	Partial	Low [5]
Selectivity	High [2] (some hydrocarbons may be retained)	Medium [3] (hydrocarbons may be absorbed)	None (undistinguished condensation)	Technology dependent [4,5], high selectivity materials are still in development phase
Energetic requirements	Medium: 27.5 kJ/kg $_{water}$ [3]	Low: 13 kJ/kg $_{water}$ [3]	Low - Very high (depends on process) [3]	Very high (if no large pressure drop is available)
Initial investment	Medium (2–3 times glycol absorption) [3]	Low (2–3 times less than PTSA)	Very low – Very high (depends on process)	Inconclusive (few reports in literature)
Operational problems	Non-steady state, fouling (green oil)	Contamination & buildup, glycol entrainment	Hydrate formation [3], insufficient JT cooling, retrograde behavior	High pressure drops are needed

[1] Molecular Sieve for Natural Gas Drying (n.d.); [2] Molecular Sieve (2012); [3] Netusil & Ditl (2011); [4] Dalane et al. (2017); [5] Solution Diffusion Mechanism, n.d

4.3 CO_2 recovery

Carbon dioxide is present in the system as it can be part of the gas fed to the syngas conversion reactor. The recovery of CO_2 is required as it cannot be fed to the product work-up process and is desired so that it can be recycled back to the syngas conversion reactor. Carbon dioxide can be recovered at the beginning of the separation train (necessary for cryogenic technologies) or at the end of the process as part of the hydrocarbon recovery section.

Membranes, molecular sieves, amine washes, physical absorption systems and distillation have been considered for this application. A description of each of these technologies based on the information extracted from literature is found in *Appendix 3*. Table 4.2 (page 24) summarizes and compares the main characteristics of each. The main outcomes of the literature research are detailed hereunder.

Despite the growing number of scientific papers reporting the advantages of using membranes to recover CO_2, there is no scientific consensus regarding their applicability in industrial scenarios. Given the low partial pressure of carbon dioxide in the feed and the substantial volume of gas to be treated, very large surface areas or very high transmembrane pressures are required. Facilitated transport membranes, inorganic and mixed-matrix membranes or membrane contactors are technologies capable of handling some of the problems that classic membranes deal with, but are still found in development phase.

Molecular sieving is a widely reported technology to capture CO_2. However, the selectivity for carbon dioxide is dependent on the technology used and typical adsorbents show a preference for unsaturated hydrocarbons over CO_2, making this technology unsuitable.

Amine washes and physical absorption systems are technologies that can potentially achieve the required concentration of carbon dioxide. Hence, these are the alternatives selected based on the literature pre-screening. These technologies will be modeled and compared in the subsequent sections for further assessment.

Despite important challenges, distillation can be used to separate carbon dioxide from C_2+ hydrocarbons. Details about this technology are found in *4.6. Hydrocarbon recovery from syngas*.

4.4 Methane recovery

Methane is a by-product and must be purged to prevent build-up and, if possible, recovered to be recycled to the methane reformer reactor.

Methane is non-polar and interacts very weakly with most materials, making its recovery a challenging operation. For this reason, the separation of methane is industrially practiced by the separation of the non-methane components of the mixture. A brief technology scouting has been performed to understand the potential of novel technologies.

Adsorption, absorption, membranes, and distillation have been considered for this application. A description of each of these technologies based on the information extracted from literature is found in *Appendix 4*. The main outcome from the literature research is that technologies described are still found at low TRLs.

Table 4.2. Comparison of carbon dioxide separation technologies

Criteria	Amine washes	Physical absorption	Molecular sieves	Membranes	Distillation
State of the technology	Industrial	Industrial	Industrial (technology) / low TRL (materials)	Industrial / development phase (enhanced materials)	Industrial
Applicability to the process	Yes	Yes	Yes	Yes	Yes
Recovery of C_2	Very high	High	Very high	Medium-high [1,2]	Very high [5]
Selectivity	High [3]	Relatively low (hydrocarbon absorption) [4,5]	Low (typical adsorbents) High (low TRL)[6]	Medium-high [1,2]	High [5]
Energetic requirements	*At 1 bar & for 250000 to 10000 ppmv.*	*At 1 bar & for 250000 to 10000 ppmv.*	Low [7]	High [8] / low [2] (discord in literature)	Very high (cryogenic conditions)
Initial investment	Medium: $78 \cdot 10^{-3}$ \$/kg CO_2 removed [7] *	Medium: $104 \cdot 10^{-3}$ \$/kg CO_2 removed [7] *	Medium [9]	Medium-high [1] (8 years lifetime, large areas required)	High (distillation unit and cryogenic system)
Operational problems	Corrosion [3], contamination & buildup, amine entrainment	Contamination & buildup, glycol entrainment	Non-steady state, fouling (green oil), efficiency decreases for high number of regeneration cycles [10]	Fouling, plasticization [2,3]	In presence of light hydrocarbons from syngas and methane: vapor pressure close to ethane and methane, risk of solid CO_2 formation, azeotrope CO_2 – ethane [11]

[1] He et al. (2022); [2] Dalane et al., 2017; [3] Meng et al. (2022); [4] Miller, B. (2015); [5] Miller, B. (2010); [6] Qazvini et al. (2021); [7] Zhang et al. (2020b); [8] Hongjun et al. (2011); [9] Riboldi & Bolland (2017); [10] Hassan et al. (2022); [11] Rackley (2010)

*Conditions differ from the studied process. Comparison cannot be extrapolated to the studied process, but can be used as a reference for the study.

4.5 Hydrogen recovery

Hydrogen is consumed in the reactions that occur in syngas reactor. It can be recovered together with syngas as part of the hydrocarbon recovery process, avoiding the use of additional units. However, as hydrogen is 65 – 85 % of the molar content of the mixture, a significant amount of energy can be saved by recovering it prior to other separation units.

The feasibility of recovering this molecule from the outlet stream of a syngas conversion reactor was already studied by Soares (2022). Most strategies used to separate hydrogen from a mixture are based on non-isobaric technologies, such as molecular sieves or membranes. Membrane technologies recover hydrogen at low pressures, and it must be later re-compressed to be recycled. Hydrogen compression is energy-intensive given its low molecular weight and its high compressibility factor. This fact, together with the high flowrate of hydrogen in the process, makes the recovery of this molecule energetically unfeasible with the current technologies. Therefore, the separation of hydrogen from the main product will be performed at the end of the process together with the uncondensed gases.

4.6 Hydrocarbon recovery from syngas

Hydrocarbons are the main product of the syngas reactor and must be recovered to be further processed and obtain intermediate or consumer goods.

Membranes, fluidized sorption beds, molecular sieves and distillation have been considered for this application. A description of each of these technologies based on the information extracted from literature is found in *Appendix 5*. Table 4.3 (page 26) summarizes and compares the main characteristics of each. The main outcomes of the literature research are detailed hereunder.

Membranes and fluidized sorption beds are technologies that can recover hydrocarbons and other organic molecules from gaseous streams. However, their applicability in the industry is limited and process-dependent, with very few cases reported for streams of similar nature to the one studied.

Cryogenic distillation is energy-demanding but suitable for the separation. Methane can also be recovered using this technology if a syngas recovery column is installed. CO_2 needs to be removed before to avoid its sublimation in the process. Strategies such as Joule–Thomson expansion or turbo expansion can be combined to the distillation to decrease the energy consumption of the process.

Distillation in presence of CO_2 is possible, but it is a challenging operation because of the low operation temperature near the sublimation point of carbon dioxide, the low relative volatility between CO_2 and C_2H_6, and the azeotrope formed between these two species. The addition of an entrainer can overcome these challenges. Depending on the configuration and on the effect of the entrainer in the relative volatility between ethane and carbon dioxide, methane can also be recovered by the installation of a syngas recovery column. Another alternative to perform the distillation in presence of CO_2 is to overcome the azeotrope with a pressure swing distillation.

Cryogenic, extractive and pressure swing distillation are the alternatives selected based on the literature pre-screening. These technologies will be modeled and compared in the subsequent sections for further assessment.

Table 4.3. Comparison of hydrocarbon-syngas separation technologies.

Criteria	Cryogenic distillation	Extractive distillation	Pressure swing distillation	Molecular sieve	Fluidized sorption bed	Membrane
State of the technology	Industrial	Industrial	Industrial	Industrial (technology) / low TRL (materials)	Industrial	Industrial (technology) / low TRL (materials)
Applicability to the process	Yes	Yes	Yes	Limited (VOC removal [1]; CH_4/CO_2 separation [2])	Limited (reported for VOC removal) [1]	Limited (few sources, CO_2/ethane) [3]
Recovery of C_2	Very high [4]	Very high [4]	Very high*			
Selectivity	High [4] (with syngas recovery column) Cannot separate CH_4 from syngas without syngas recovery column (one column)	High* Cannot separate CH_4 from syngas without syngas recovery column (in some cases, cannot separate ethane from CO_2)	High* Cannot separate CH_4 from syngas without syngas recovery column			
Energetic requirements	Very high [4] (with syngas recovery column) High (with only one column)	High [4]	High*			
Initial investment	Very high [4] (with syngas recovery column) High (with only one column)	High [4]	High*			
Operational problems	—	Risk of solid CO_2 formation [5]	Risk of solid CO_2 formation [5]			

[1] Chandran et al. (2018); [2] Radique et al. (2015); [3] Nyce et al. (2015); [4] Soares (2022); [5] Rackley (2010)

*Based on extractive distillation literature (Soares, 2022)

5 TECHNOLOGY DEVELOPMENT & PROCESS MODELLING

Heuristic calculations and *Aspen Plus V11* have been used to model the alternatives selected. The criteria to choose between heuristics and software is both the competence of the software to perform simulations of certain physical phenomena and the complexity of such simulations.

5.1 Software modelling with *Aspen Plus*

The simulation setup of the simulations using Aspen with property methods that have been customized based on Dow internal research and operational expertise.

Common blocks that are used in most models have been simulated similarly. To simplify matters, the specifications of all these blocks are consolidated in Table 5.1.

Table 5.1. Specification of common blocks in the simulations.

Unit	Block	Configuration / Parameters used
Pump	*Pump*	Efficiency: 0.6
Expansion valve	*Valve*	Adiabatic
Heat exchanger	*Heater*	Pressure drop: 0.2 bar
Knock-out drum	*Flash2*	Adiabatic
		Pressure drop: 0.1 bar
Centrifugal compressor	*Compr*	ASME polytropic method
		Polytropic coefficient: 0.8
		Mechanical efficiency: 0.985
Multistage centrifugal compressor	*MCompr*	ASME polytropic method
		Polytropic coefficient: 0.8
		Mechanical efficiency: 0.985
		Number of stages dependent on the design
Turbine	*Compr*	ASME method
		Isentropic coefficient: 0.855
		Mechanical efficiency: 0.985
Molecular sieve	*Sep*	Remove all water content (experience shows extremely high selectivity and efficiency)
Reboiled stripper	*RadFrac*	Reboiler (Kettle) but not condenser*
		Number of stages dependent on the design
		One degree of freedom: dependent on the design
Reboiled stripper with rectification	*RadFrac*	Reboiler (Kettle) and condenser (partial-vapor)*
		Number of stages dependent on the design
		Two degrees of freedom: dependent on the design

Table 5.1. Specification of common blocks in the simulations. (cont.)

Unit	Block	Configuration / Parameters used
Distillation column	*RadFrac*	Reboiler (Kettle) and condenser (partial-vapor/total)*/**
		Number of stages dependent on the design
		Two degrees of freedom: dependent on the design
Absorption column	*RadFrac*	No reboiler nor condenser
		Number of stages dependent on the design

* Kettle reboiler is not usually the preferred option due to their high cost, their operational problems and their tendency to collect and accumulate solids and impurities. However, it is used in the simulations to help convergence.

**Total condenser is only used if the distillate does not need to be in gaseous state

The energy consumption of all the models described in section *5. Technology development & process modelling* has been calculated. For this purpose, the following items have been considered:

- Cooling duty: is the result of the addition of the energetic requirements of all the heat exchangers and condensers of distillation columns. To be able to add up the cooling demand for different temperatures, all duties have been converted to electrical energy. The weighting factors used are found in Table 5.2 (page 29). Cases where the energy consumption of cooling duty has been neglected are:
  - Heat exchangers that exchange energy between two streams of the process.
  - Air refrigerants, as they consume an insignificant amount of electricity when compared to refrigeration cycles
  - Cooling water at more than 35 ºC, as tower water consume an insignificant amount of energy when compared to refrigeration cycles
  - Heat exchangers cooling down at temperatures higher than 100 ºC, as the refrigeration can be achieved using boiler feed water.
- Compressor power: the electrical power is obtained as a direct result of the simulation. Power consumed by compressors linked to turbo-expanders is not considered.
- Pumping power: the electrical power is obtained as a direct result of the simulation.
- Reboiler duty: the thermal power is obtained as a direct result of the simulation.

To compare the energy consumed by the different equipment, all energies have been converted to mass of fuel (methane) equivalent. The weighting factors used are 0.34 for electrical power and 0.85 for thermal power.

A pinch analysis of the processes modelled was not conducted due to time restrictions, so temperature cross-over may take place in some parts of the process.

Table 5.2. Electric power consumption of refrigeration cycles.

Refrigerant cycle	Refrigerant temperature [ºC]	Compressor duty required [$kW_{electricity}/kW_{refrigerant\ duty}$]
Propylene	10.	0.176
	-40.	0.458
Ethylene	-60.	0.747
	-80.	0.888
	-100.	1.076
N_2/CH_4	-150.	2.150

An economical assessment is performed in some models as they require additional assessment to support the energy consumption analysis.

CAPEX is calculated using the Aspen Integrated Economics extension (1st quarter 2018 pricing basis). The cost of multi-stream plate fin heat exchangers is calculated using the *MHeatX* block. Due to the lack of inputs for heat exchangers, their capital cost is calculated using internal equipment cost models developed by Dow.

OPEX is calculated using the fuel consumption equivalent (natural gas) and its cost, obtained from the LTHV list. An operation time of 90 % is considered for the calculation.

The total annualized cost is calculated with the objective to combine CAPEX and OPEX in a single economic indicator. CAPEX inversion is distributed in a time period of 15 years.

5.2 Water removal

5.2.1 Molecular sieves

The system has been modelled with a combination of heuristics and simulations.

The model consists of 3 molecular sieve columns operating in parallel: two operate online and one in regeneration. TSA has been chosen for this application among the typical strategies for a semi-continuous operation, as the working capacity of the catalyst is strongly dependent on temperature. Details about how molecular sieves work and their typical operational approaches can be found in *Appendix 2*.

Feed conditions and composition depend on the flowsheet of the process. Two scenarios are considered:

- TSA is the first unit operation
- Carbon dioxide is recovered before the TSA using an amine wash system

In the first scenario, the concentration of the stream is the one described in Table 2.1. In the second scenario, the concentration of CO_2 has been reduced to 50 ppmv and the stream has been saturated with water at the operating conditions of the amine wash.

Figure 5.1 illustrates the model developed for the dehydration process of the studied stream (first scenario described).

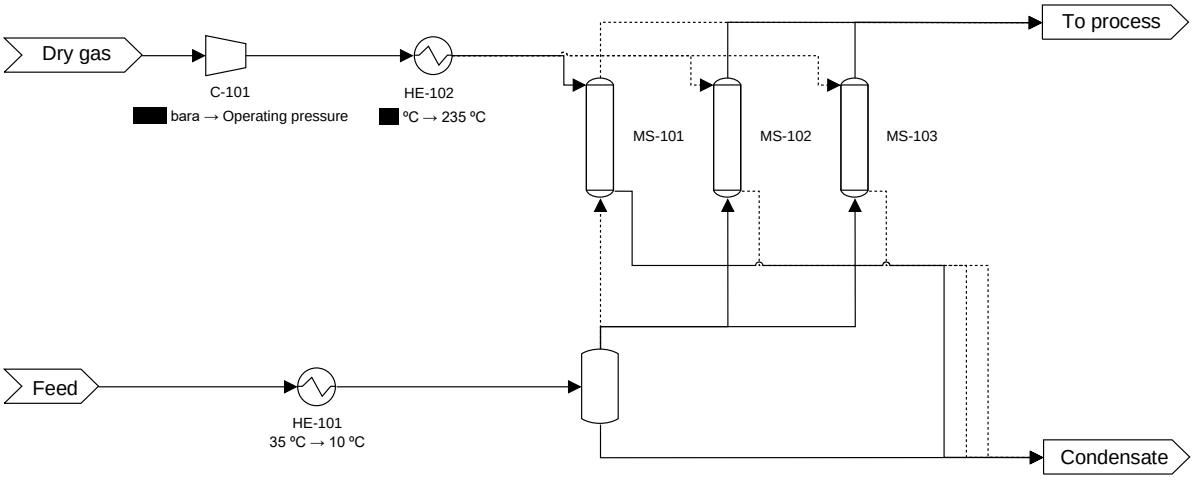

Figure 5.1. Model for TSA.

The feed stream is cooled down to 10 ºC to enhance adsorption in the molecular sieves and condensed water is knocked out. The stream is split and sent to columns *MS-102* and *MS-103*. After water has been removed, the stream is sent to the next unit operation.

The molecular sieve MS-*101* is operating in regeneration mode using dry process gas that contains no olefins. The gas is compressed to bring the stream to the operating pressure of the unit. The temperature is increased to a regeneration temperature of 235 °C (Khol & Nielsen, 1997) and then sent to the column being regenerated. The use of the wet gas after regenerating the column will depend on the nature of the dry gas stream.

Molecular sieve columns have been dimensioned as following:

1. Selection of adsorption catalyst. The chosen model absorbent for the analysis is 2.05 mm BASF 3A Molecular Sieve (BASF Catalysts LLC, n.d.).
2. Calculation of the mass of the catalyst. Assuming an operation of 72 h, the total mass of water that needs to be adsorbed is calculated. To obtain the mass of catalyst, its overall adsorption capacity has been approximated to its equilibrium capacity. Additional approximations are: neglection of the exothermicity of adsorption, neglection of the adsorption capacity loss due to aging, and no overdesign to avoid sudden breakthrough.
3. Calculation of the feed mass surface velocity. Given an arbitrary column diameter, the mass surface velocity is calculated using the volumetric flow at the working conditions and the density of the stream.

4. Calculation of the average bed porosity using Benyahia & O'Neill correlation for spherical particles (2005).

$$\Phi = 0.39 + \frac{1.74}{\left(\frac{\emptyset_{column}}{\emptyset_{catalyst}} + 1.14\right)^2}$$

5. Calculation of the apparent density of the bed using the average bed porosity and the catalyst bulk density.
6. Calculation of the apparent volume of the catalyst using the apparent density and the mass of catalyst.
7. Calculation of the column height using the apparent volume of catalyst and the diameter of the column. A flat concentration profile in the column is assumed to simplify the calculation, so no unused bed length is used. Additional height of inert spheres to avoid sieve tray blocking by the catalyst has also been considered in the calculation. A layer of 6" of thickness of ½ inch spheres is placed just after the trays, and another layer of 6" of thickness of ¼ inch spheres is placed just before the catalyst. As there is one tray at the bottom and another tray at the top, a total of 24" of height is needed to stack the inert spheres. According to Khol & Nielsen (1997), ratios height/diameter of the column of 2/1 to 5/1 are preferable.
8. Pressure drop calculation using Ergun equation.

$$\frac{\Delta P}{\Delta z} = -\frac{4}{\pi} \frac{Q}{\emptyset_{column}^2 \cdot \emptyset_{catalyst}} \cdot \left(\frac{1-\Phi}{\Phi^3}\right) \cdot \left(\frac{150 \cdot (1-\Phi) \cdot \mu}{\emptyset_{catalyst}} + \frac{7}{\pi} \cdot \frac{Q}{\emptyset_{column}^2} \cdot \rho_{gas}\right)$$

9. Iteration of the column diameter until obtaining an acceptable pressure drop (0.1 bar).

To calculate the required flowrate to regenerate the adsorption columns, the methodology suggested by Khol & Nielsen (1997) has been used. Three differentiated steps are needed to regenerate a column: pre-regeneration (to increase the temperature of the column from operation to regeneration conditions), regeneration (to desorb the water from the catalyst) and cooling (to decrease the temperature of the column from regeneration to operation conditions). The following steps have been followed:

1. Calculation of the heat needed for pre-regeneration. In this step, the temperature of both the catalyst and the vessel needs to be increased. The necessary heat to raise the temperature of the catalyst is calculated using its mass and its heat capacity ($0.92 \frac{\text{kJ}}{\text{kg ºC}}$, according to Khol & Nielsen, 1997). The heat needed to increase the temperature of the vessel is calculated using its mass (estimated using Arc Energy's tool, 2021) and the heat capacity of stainless steel ($0.5 \frac{\text{kJ}}{\text{kg ºC}}$). Heat losses of 10 % are assumed. Moreover, experience shows that only part of the heat supplied is used during operation. Khol & Nielsen (1997) estimate that only half of the total heat supplied is utilized, so the energy provided must be twice the one calculated.

2. Calculation of the regeneration heat using the total mass of water adsorbed in the column and a desorption heat of 4186.8 $\frac{kJ}{kg}$ (Khol & Nielsen, 1997). All the water adsorbed in the column is assumed to be desorbed during this step.
3. Calculation of the heat that needs to be dissipated for cooling the column. It is analogous to step 1 but decreasing the temperature.

When comparing the results of the heat needed for the different steps, it is observed that the energy required for each is of the same order of magnitude. Pre-regeneration is performed in 8 h, regeneration in 12 h and cooling in 6 h. As a constant flowrate of regeneration gas is expected, and the step with a lower operation time is cooling, the higher power consumption will come from the cooling step. As the cooling flowrate is the one that limits the whole regeneration flowrate, it wis the one used in the energy consumption calculation of the system.

4. Calculation of the cooling gas flow using the total heat to be dissipated, the regeneration gas heat capacity and the time to cool down the column.

The energy consumption of the system is reduced to the compression and heating of the regeneration gas and to the cooling of the feed stream. Duty to bring the regeneration gas from the process temperature to 10 ºC is not considered.

5.2.2 Glycol absorption

Simulation software has been used to model this technology using a design based on Netusil & Ditl (2011). Among the typical glycols for glycol absorption dehydration, TEG has been the chosen one for its high boiling point (decreasing vaporization loss and operating costs) and for its high decomposition temperature (Dalane et al., 2017). Details about how glycol absorption works and its typical operational approach can be found in *Appendix 2*.

Feed conditions and composition depend on the flowsheet of the process. Both scenarios presented in *5.2.1. Molecular sieves* are considered in the model.

Figure 5.2 illustrates the model developed for the dehydration process of the studied stream (first scenario described).

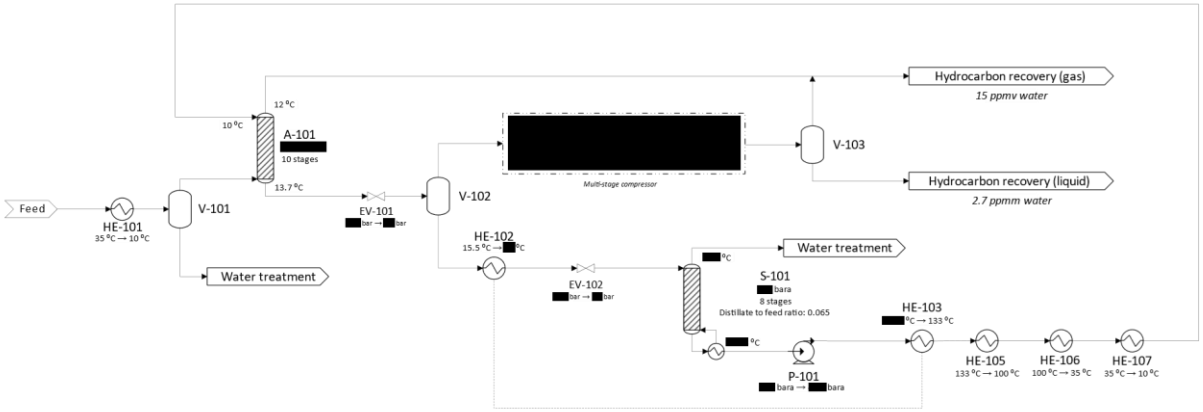

Figure 5.2. Model for glycol dehydration (omitted solvent make up stream).

The feed stream is cooled down to 10 ºC to improve absorption efficiency in the column and condensed water is knocked out. The stream is sent to the absorption column *A-101* and fed at its bottom, while glycol is fed at its top. Solvent flowrate is chosen to minimize the concentration of water in the dry gas. The glycol absorbs water from the gas while flowing downward through the column. The dehydrated gas is sent to the next unit operation.

Wet glycol is sent to regeneration. The stream is depressurized in two stages: the first brings the stream to [redacted] bara and the second to [redacted] bara. The first pressure is set to minimize the concentration of water in the vapors generated during the decompression while still recovering absorbed hydrocarbons. The vapor stream is recompressed back to the inlet pressure using a multistage compressor. Condensate is knocked out and sent to hydrocarbons recovery.

Low-pressure wet glycol is fed to a recovery column (reboiled stripper). Design specifications provide a concentration of water in the regenerated glycol of [redacted] $\%_w$ to avoid excessively high temperatures in the reboiler. The regenerated solvent is repressurized and cooled down to the absorption column operating conditions. This recycle uses part of its energy to pre-heat the wet glycol with the objective to decrease the reboiler duty of *S-101*.

It is worth highlighting the very low pressure at which *S-101* is operating. The reason behind it is that, during the design, temperatures above the decomposition temperature of TEG were reached. To solve this challenge without using alternative designs, two solutions were considered: increasing the concentration of water in the lean glycol and decreasing the pressure.

- Decrease the purity of the solvent: as the boiling point of water is significantly lower than that of TEG, increasing the concentration of water in the solvent would result in a decrease of the boiling temperature below the glycol decomposition temperature. However, as the concentration of water in the treated gas depends on the humidity of the lean glycol, decreasing the purity of the solvent leads to an enormous increase of the humidity in the dry gas. Equilibrium in *A-101* is quickly achieved, so the increment of solvent flowrate to decrease again the concentration of water in the dry gas is enormous. In fact, that is the reason why dry gas does not achieve the specified constraints: an increase of the solvent flowrate to achieve the required concentration results on a marginal reduction of water in the treated gas.
- Decrease the operation pressure of the column: by doing so, the boiling point of the glycol in the reboiler decreases below its degradation temperature, allowing the separation. Although the operation of this equipment under these conditions is not pragmatic nor realistic, it is in theory able to perform the operation.

Gas stripping or enhanced regeneration units like Drizo's® & Coldfinger's® designs can overcome the challenges already mentioned (Netusil & Ditl, 2011). However, an in-depth study of these enhanced technologies is outside of the scope of the project, and are therefore not evaluated in the current work.

Results show that large amounts of hydrocarbons are absorbed by the glycol and lost in the dehydration process. For this reason, further recovery can be implemented after the regeneration column. Figure 5.3 illustrates the model developed for the additional recovery.

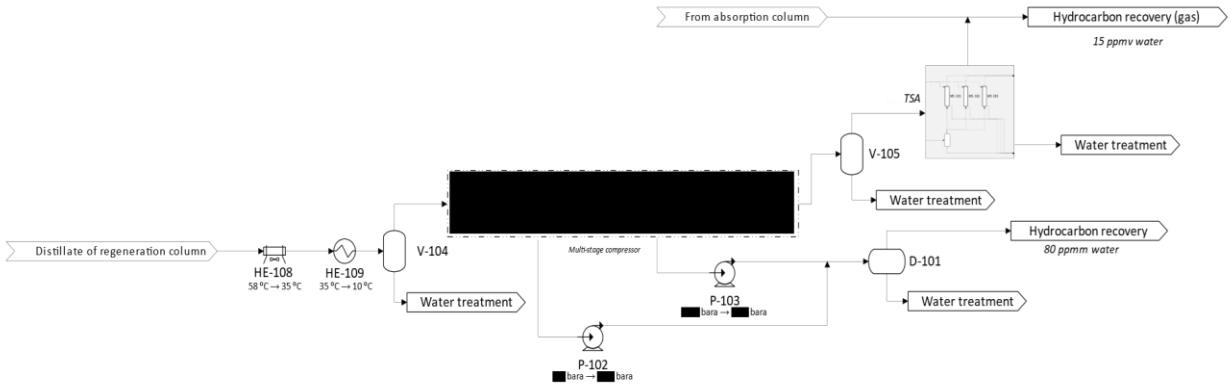

Figure 5.3. Model for glycol dehydration (additional hydrocarbon recovery).

Distillate from the regeneration column is cooled down, to 10 ºC and condensed water is knocked out. The stream is recompressed back to the inlet pressure using a multistage compressor. Interstage condensate is rich in hydrocarbons, so the stream is decanted to recover them. The condensate coming out of the last stage (mainly water) is knocked out and the gas is sent to a molecular sieve to remove water remaining in the stream.

Although this alternative also uses TSA, the sizes of the molecular sieves are significantly smaller because most part of the water has already been removed.

5.3 CO_2 recovery

5.3.1 Amine washes

The system has been modelled combining internal methodologies developed by the Dow Industrial Solutions R&D and simulations.

The model is based on a typical amine wash system with both partial and complete regeneration of the solvent. Details about how this system works and its typical operational approaches can be found in *Appendix 3*. The greatest difference between the system described in the literature review and the model is the absence of a high-pressure flash. As the partial pressure of CO_2 in the stream is very low, its depressurization results in a negligible desorption of carbon dioxide.

Figure 5.4 (page 35) illustrates the model developed for the carbon dioxide recovery process of the studied stream (first scenario described).

The feed stream is sent to the absorption column *A-101* and fed at its bottom, while the amine solvent fed at its top (at different stages). To simulate the properties of the solvent, a Dow proprietary amine solvent was used in the models. Solvent flowrates (lean and semi-lean) are chosen to remove the CO_2 from the gas while minimizing the energy consumption of the regeneration column. The solvent physically and chemically absorbs carbon dioxide from the gas while flowing downward through the column and he treated gas is sent to the next unit operation. Complete removal of CO_2 from the gas is assumed.

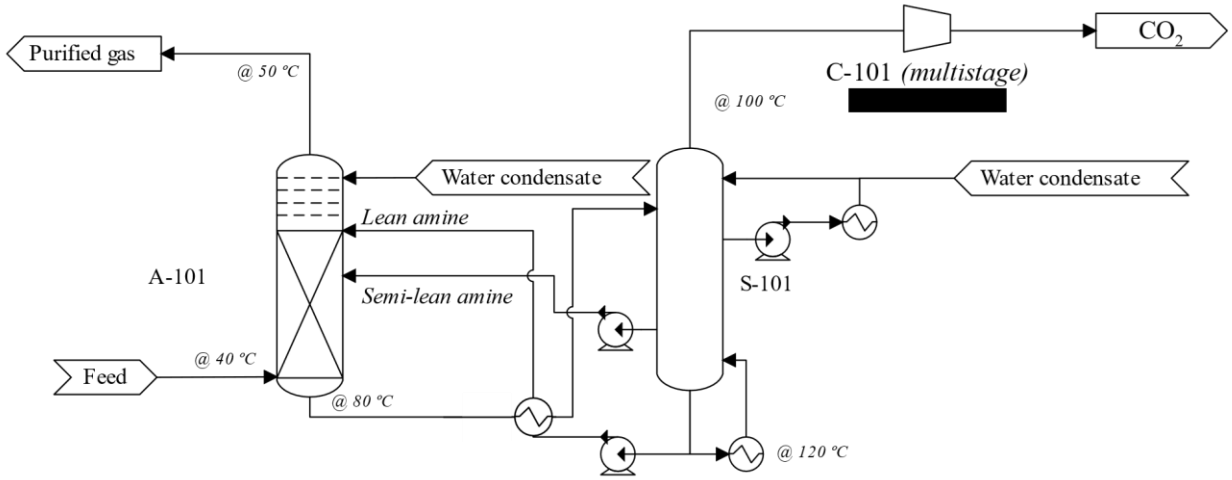

Figure 5.4 (a). Model for amine wash (omitted solvent make up stream).

[Figure deleted for confidentiality purposes]

Figure 5.4 (b). Schematic of the multistage compressor for the amine wash.

Rich solvent is pre-heated and sent to regeneration in a reboiled stripper. One of the most important design specifications of this unit is the volumetric ratio of lean to semi-lean. Low ratios reduce the energy consumption of the reboiler (as only low fractions of the total solvent flowrate are regenerated) but increase the total flowrate necessary to absorb the required amount of CO_2, increasing the pump energy consumption. This ratio is optimized by the designer based on the carbon dioxide partial pressure in the feed and the minimization of total energy input. Solvent is recycled to *A-101*.

The CO_2 recovered can be pressurized for carbon utilization or sequestration. In order to do so, it must be recompressed using a multi-stage compressor with inter stage cooling.

5.3.2 Physical absorption

The system is modelled using simulation software. Among the typical strategies for this operation, Rectisol® is the chosen one. Models developed for other technologies presented solvent interaction issues with the property database. Details about how technologies based on physical absorption of CO_2 work and their typical operational approaches can be found in *Appendix 3*.

The studied scenario considers a previous water removal unit, so the feed is dehydrated and at a temperature of 10 °C.

Figure 5.5 illustrates the model developed for the carbon dioxide recovery process of the studied stream.

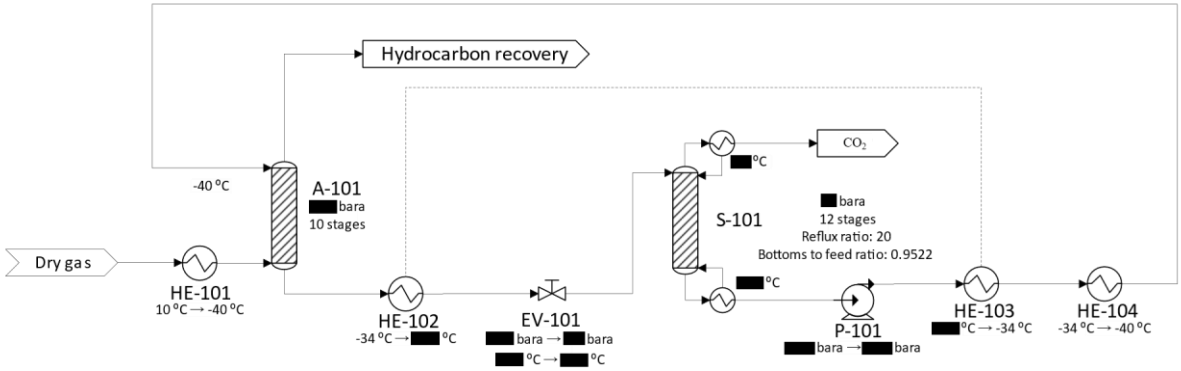

Figure 5.5. Model for Rectisol® CO_2 recovery (omitted solvent make up stream).

The feed stream is cooled down to the operation temperature. The stream is sent to the absorption column *A-101* and fed at its bottom, while the solvent is fed at its top. Solvent flowrate is chosen to reduce the concentration of CO_2 in the gas to 50 ppmv. Methanol absorbs water from the gas while flowing downward through the column and treated gas is sent to the next unit operation.

Rich solvent is sent to regeneration. The stream is depressurized and fed to a recovery column (reboiled stripper with rectification). Design specifications provide a concentration of carbon dioxide in the regenerated methanol of [redacted] $\%_w$ n-butane ([redacted] $\%_w$ C_2+) and a condenser temperature of 10 °C. Both settings are defined to reduce the energy consumption of the column while still providing regenerated solvent of good quality. The regenerated solvent is repressurized and cooled down to the absorption column operating conditions. This recycle uses part of its energy to pre-heat the rich methanol with the objective to decrease the reboiler duty of *S-101*.

Results show that large amounts of hydrocarbons are absorbed by methanol and lost in the CO_2 recovery process. Unlike in the case of glycol absorption (*5.2.2. Glycol absorption*), further recovery cannot be implemented after the regeneration column due to the azeotrope ethane-carbon dioxide.

5.4 Distillation

5.4.1 Cryogenic distillation

Cryogenic distillation for the recovery of olefins from syngas has been studied by Soares (2022).

The author suggests two alternative designs for this separation. The first design is based on Al-Qahtani et al. (2017) work and consists of a cold box system, a demethanizer unit and a syngas recovery column. The second design removes the syngas recovery column, eliminating the possibility of recovering methane from syngas and inert gases.

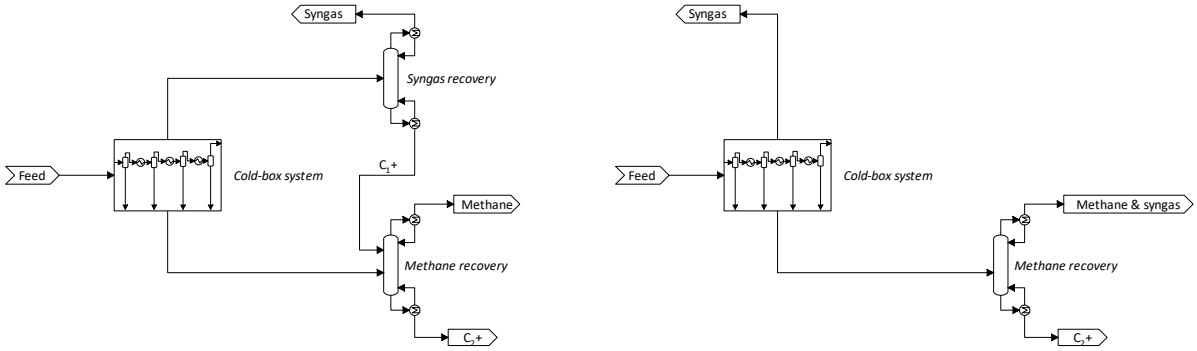

Figure 5.6. Designs based on Al-Qahtani et al. (2017) (left) and design modified without the syngas recovery column (right).

Results from Soares (2022) show that the design based on Al-Qahtani et al. (2017) work has an energy consumption 150 to 220 % higher than the design without the syngas recovery column. The two main reasons to separate methane from the syngas is so that it can be recycled to a methane reformer reactor and to avoid purging syngas when purging methane to prevent its build-up.

- Regarding the separation for recycling, the recovery of methane that can be achieved by using two distillation columns is, at most, 5 % of the fresh methane fed to the methane reformer. This small percentage that can be recycled does not justify the increment of energy compared with the scenario with no methane recovery.
- When it comes to avoid losing syngas with the purge, given the small amount of methane that must be removed from the process to prevent build-up, very few syngas is lost.

Therefore, only the design with one distillation column is analyzed in this project.

The cold box system is based on a cascaded refrigeration system that provides cooling duty until -100 ºC. To achieve acceptable C_2 recoveries, temperatures of around -150 ºC are required. Two different refrigeration strategies to achieve cryogenic temperatures are studied by Soares (2022). The first strategy consists of the expansion of the cascade system to reach -150 ºC by using a mixed refrigerant (mainly N_2 & CH_4). The second strategy consists of the turbo-expansion of the process stream to reduce its temperature.

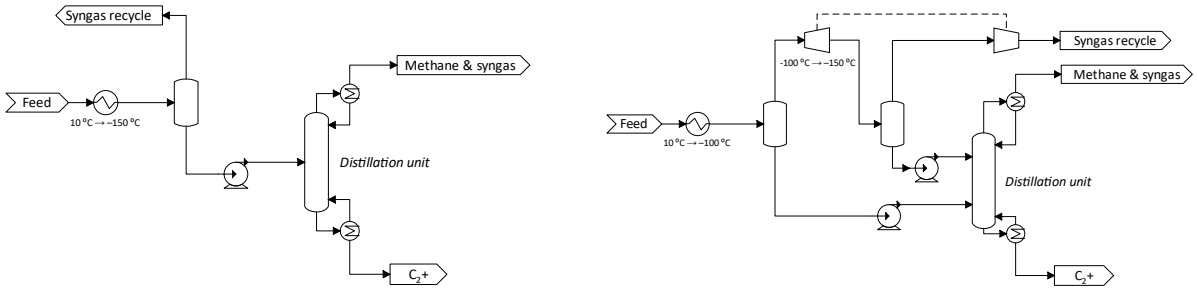

Figure 5.7. Refrigeration strategies studied by Soares based on mixed refrigerant (left) and based on process stream turbo-expansion (right).

Soares' results (2022) show that the energy consumption of the alternative that uses mixed refrigerant is 30 % higher than that of the alternative that uses the process stream turbo-expansion. These results are expected to differ from the ones for the paraffins recovery due to the differences in the feed composition: rich in olefins for Soares (2022) vs rich in paraffins for the current work. For that reason, both refrigeration strategies have been studied in the current work to determine which configuration has the lowest energy consumption.

The cold box system is simulated as a sequence of heat exchangers and knockout drums. It can be sectioned into different stages, each providing a temperature decrease of 20 – 30 ºC to avoid thermal stress.

Each stage consists of a cooling section and a knock-out drum (see Figure 5.8).

The cooling section contains one or two pre-coolers and a cooler. Pre-coolers decrease the temperature of the stream using the cold syngas recycle to improve the energy efficiency of the system. Coolers decrease the temperature until the objective temperature of that cooling section. The knock-out drum separates the liquid that has condensed from the gas.

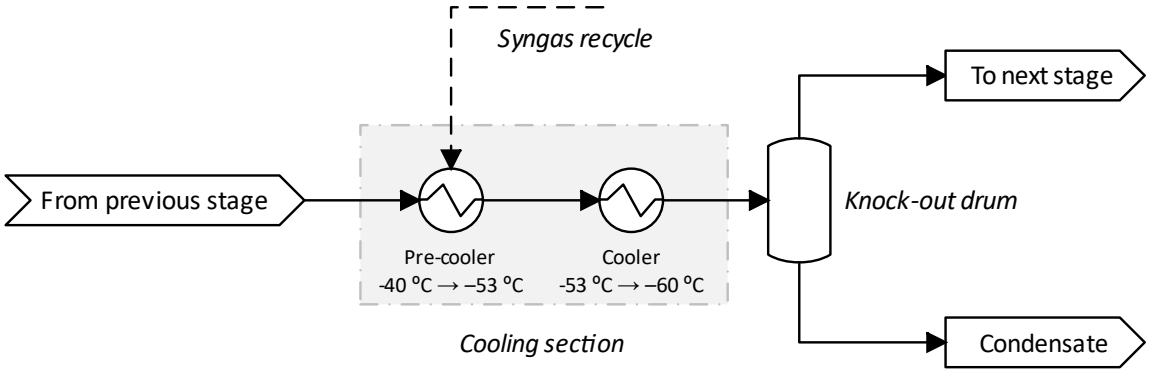

Figure 5.8. Scheme of a stage from the cold box.

The temperature drop of each stage is given by the temperature of the refrigerants available. Propylene and ethylene refrigeration cycles are currently installed in the plant. With propylene cycles, temperatures of 10 ºC and of -40 ºC are achievable. With ethylene cycles, -60 ºC, -80 ºC and -100 ºC can be used. With mixed refrigerant cycles or turbo-expanders, temperatures of -150 °C are achievable.

A total of 22 configurations have been analyzed to select the option with the lowest energy consumption option for each of the refrigerant strategies.

Figure 5.9 (page 39) illustrates the model developed for a base case operation using mixed refrigerant. Guidelines to understand the figures and the model are:

- Each cooling section of the cold box is represented as a single heat exchanger, even though its simulation consists of a pre-cooler and a cooler, as described in Figure 5.8.
- Unit HE-1XX represents a series of exchangers.

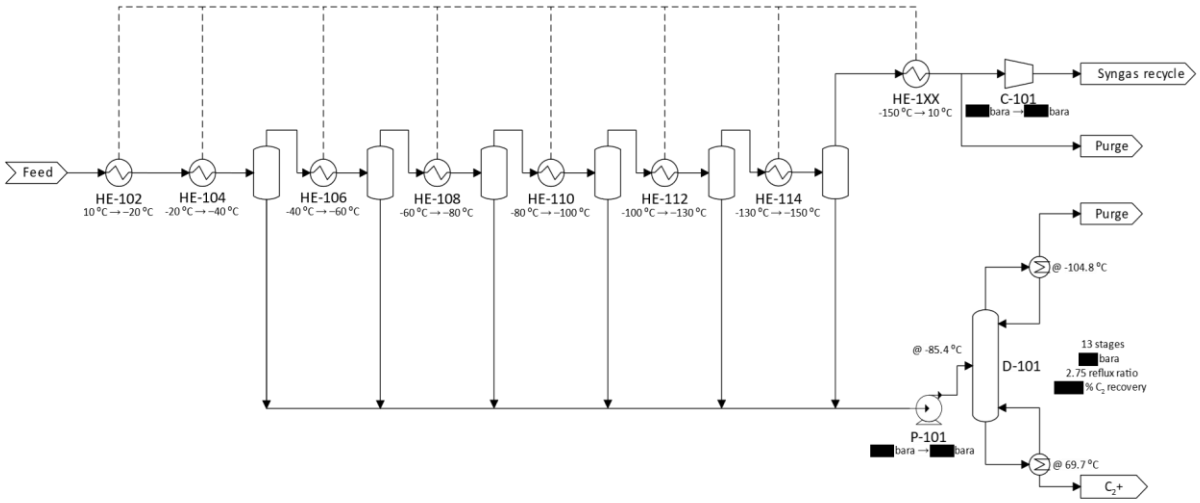

Figure 5.9. Model for cryogenic distillation: configuration 1.1.

The feed stream is fed to the cold box and cooled down to -40 °C. At this temperature, hydrocarbons start to condense and are knocked out. The uncondensed gas is sent to the next cooling section of the cold box and the process is repeated until the gas is cooled down to -150 °C. Uncondensed gas is heated, compressed, and sent back to the reactor. This recycle uses part of its energy to pre-cool the stream fed to each section of the cold box.

Condensed hydrocarbons are pressurized and fed to a distillation column that acts as a demethanizer. Some design decisions taken when modelling the column are:

- An operating pressure close to the inlet pressure is chosen to avoid non-isobaric processes. For some of the configurations studied, the pressure has been modified to achieve other column specifications.
- The temperature of the feed is aimed to be close to that of the saturated liquid to facilitate the operation. A subcooled feed would help in the separation, but the temperatures required would need additional refrigeration, substantially increasing the energetic demand.
- Reflux rate and the number of theoretical stages have been chosen according to a sensitivity analysis performed to minimize the condenser duty.
- The feed stage has been chosen to favor the separation and avoid potential hydrodynamic problems.

Design specifications provide a minimum recovery of ethane in the column of [redacted] % (although higher recoveries are aimed) and a maximum concentration of CO in the product of 1000 ppmm.

The stream obtained at the bottom of *D-101* is the main product (C_2+).

As described in *2.2. Basis of engineering*, methane and nitrogen must be purged to prevent build-up. Both purges have been located at the streams with a higher methane/nitrogen to CO ratio to avoid the loss of reactant and the loss of product. The best stream to be used as purge is the

distillate from *D-101*. However, the quantity of methane/nitrogen purged is not enough to achieve the specifications of the process. For that reason, the remaining mass of methane/nitrogen to achieve the requirements is purged from the syngas recycle.

The pressure of both purges is above 20 bara and the temperature of the distillate stream is below -100 ºC, opening the door to an energetic utilization of these streams.

The syngas recycle purge is rich in H_2, so a PSA cycle can be used to recover this reactant and recycle it back to the reactor. If the stream is expanded to reduce its temperature and is used to decrease the cooling duty of the cold box system, the hydrogen obtained after the PSA cycle must be re-compressed to be fed to the reactor and the electrical consumption of the system substantially increases. For this reason, this stream is not further utilized to decrease the energetic demand of the operation, and only used with the objective of recovering the hydrogen present. Hydrocarbons that can be recovered in this purge can be thermally revalorized.

In the case of the distillate purge, the stream is rich in CH_4 and can be sent to a methane reformer. To do so, the stream must be heated up to 20 ºC, so the stream can be used to decrease the cooling duty of the cold box system. An elevated feed pressure is preferred for the methane reformer, therefore a limit exists on the isenthalpic expansion that can be performed to further decrease the temperature and help on the system cooling duty reduction. For the same base case using mixed refrigerant, the implementation of this system is shown in Figure 5.10.

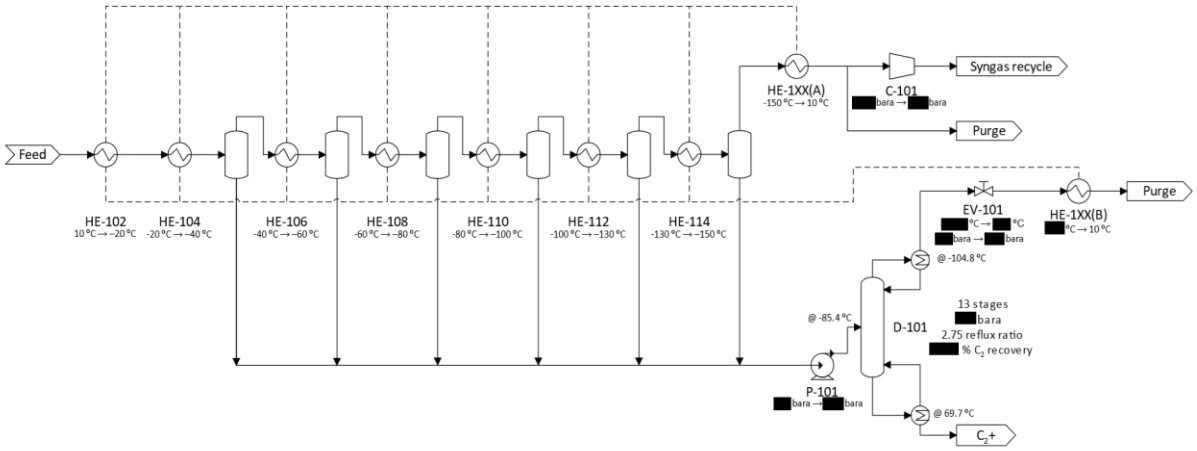

Figure 5.10. Schematic of cryogenic distillation: configuration 1.2.

Figures from 5.11 to 5.20 illustrate the models developed for other configurations.

All the configurations shown have been analyzed with and without the utilization of the distillate purge to reduce the cooling duty of the cold box. For the sake of simplicity, only the figures of the alternatives without this energy integration have been included in the report.

For each configuration, the reference *X.1* refers to the configuration without the utilization of the distillate purge to reduce the cooling duty of the cold box and the reference *X.2* refers to the configuration with this energy integration; where *X* is the number of the configuration.

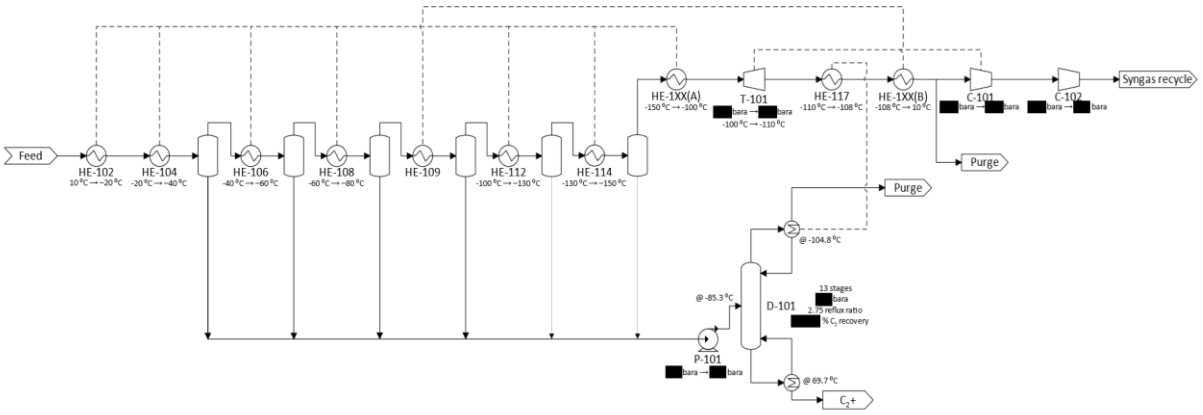

Figure 5.11. Schematic of cryogenic distillation: configuration 2.1

As the condenser duty requires the use of mixed refrigerant, an alternative refrigeration method has been suggested. Instead of using refrigerant, this configuration aims to use the process stream as coolant in the condenser. In this case, the syngas recycle has been thermally integrated down to -100 ºC (so that the pre-cooling of *HE-112* and *HE-114* remains unaltered). Then, the stream is expanded in a turbine to decrease its temperature down to -110 ºC so that there is an additional differential of temperature to allow effective heat exchange. The stream is then used to generate the reflux of the column, and with the remaining energy, is thermally integrated with the rest of the cold box.

By using this configuration, refrigeration duty at -100 ºC is unnecessary, as the temperature is provided by the pressure drop in the turbo-expander.

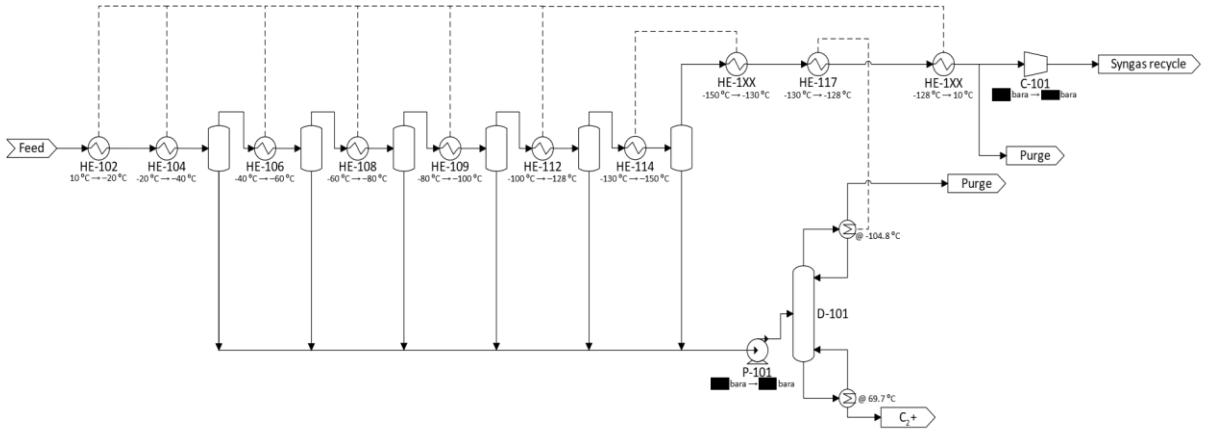

Figure 5.12. Schematic of cryogenic distillation: configuration 3.1.

In the case of configuration 3.1, the syngas recycle has been thermally integrated down to -130 ºC to supply cooling duty to the condenser. This way, the pre-cooling of *HE-114* remains unaltered. Then, the stream is used to generate the reflux of the column, and with the remaining energy, is thermally integrated with the rest of the cold box.

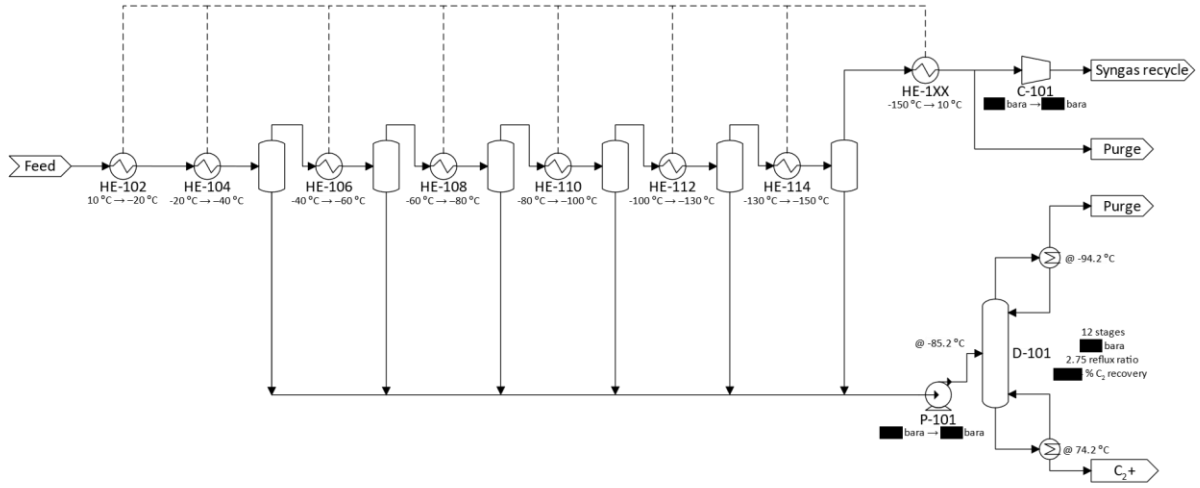

Figure 5.13. Schematic of cryogenic distillation: configuration 4.1.

For this configuration, the operating pressure of the column has been increased to raise its overall temperature. By doing so, the condenser temperature increases, and the duty required is of -100 ºC instead of -150 ºC. The design of the column has been modified to achieve similar performances to the previous configurations.

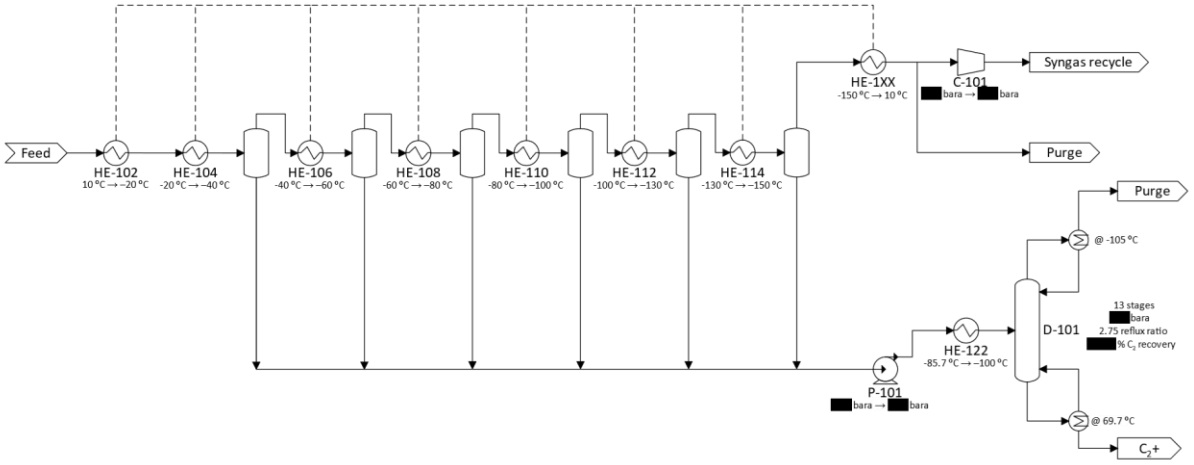

Figure 5.14. Schematic of cryogenic distillation: configuration 5.1.

This is a modification of the configuration 1.1. Feed pre-heating is commonly used in distillation columns to reduce the reboiler duty at the expense of increasing the condenser duty. In this process, as the condenser is operating at very low temperatures, its duty is prioritized over the reboiler to reduce the overall energy consumption. Therefore, and oppositely to the scenario where reboiler duty aims to be reduced, a pre-cooler is installed at the feed of the column.

The stream is cooled down to -100 ºC, as cooling it down to lower temperatures would require duty at -150 ºC (decreasing the condenser duty, but increasing the pre-cooler duty).

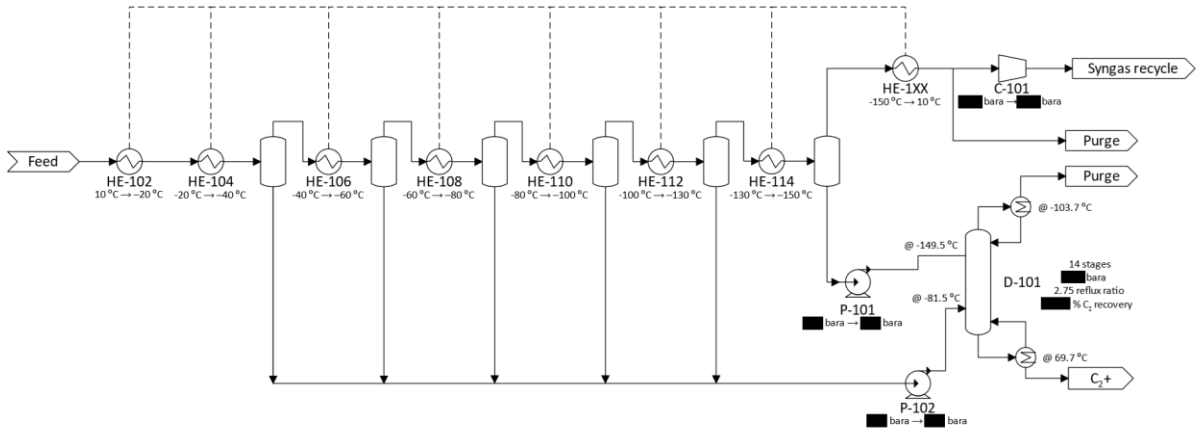

Figure 5.15. Schematic of cryogenic distillation: configuration 6.1.

Feed splitting is used together with pre-cooling to reduce the energy consumption of cryogenic distillation towers. This technique consists of splitting the feed and pre-cooling one or more of the new streams obtained before being fed to the column. By doing so, the condenser duty decreases (as it is aimed in configuration 5.1), but the energy consumption of the pre-cooler is reduced, as only a fraction of the total stream is cooled.

Due to the structure of the cold box, different streams with different temperatures are obtained. As the last stream obtained in the cold box is already at -150 °C, there is no need of pre-cooling it.

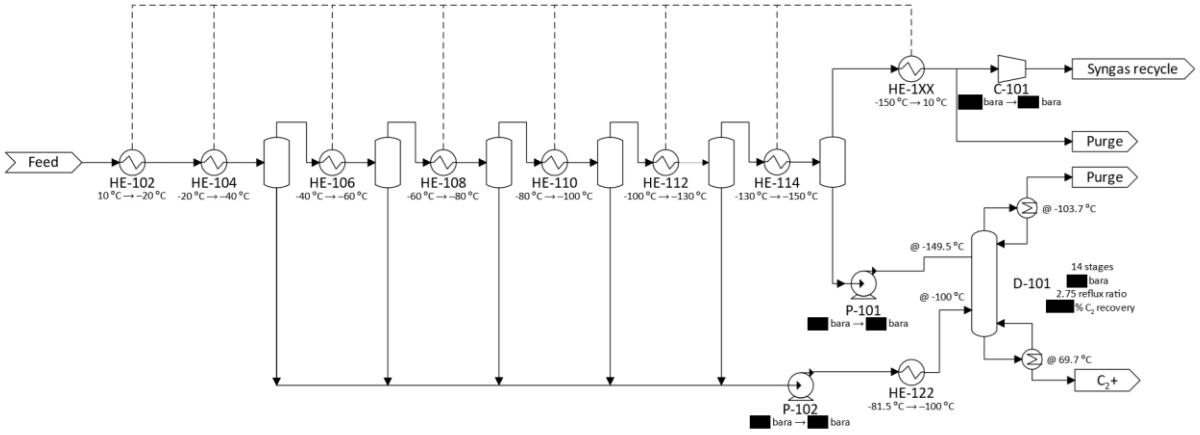

Figure 5.16. Schematic of cryogenic distillation: configuration 7.1.

For this case, configuration 6.1 has been modified. After feed-splitting the stream that enters the distillation column, a pre-cooler is installed after *P-102*. This stream is the result of collecting all the condensed hydrocarbons from the cold box system, except for the stream coming from the last knock-out drum at -150 °C.

This configuration aims to further decrease the energy consumption of the condenser by pre-cooling one of the streams that is fed to the column, at a higher temperature than the one coming from the last knock-out drum.

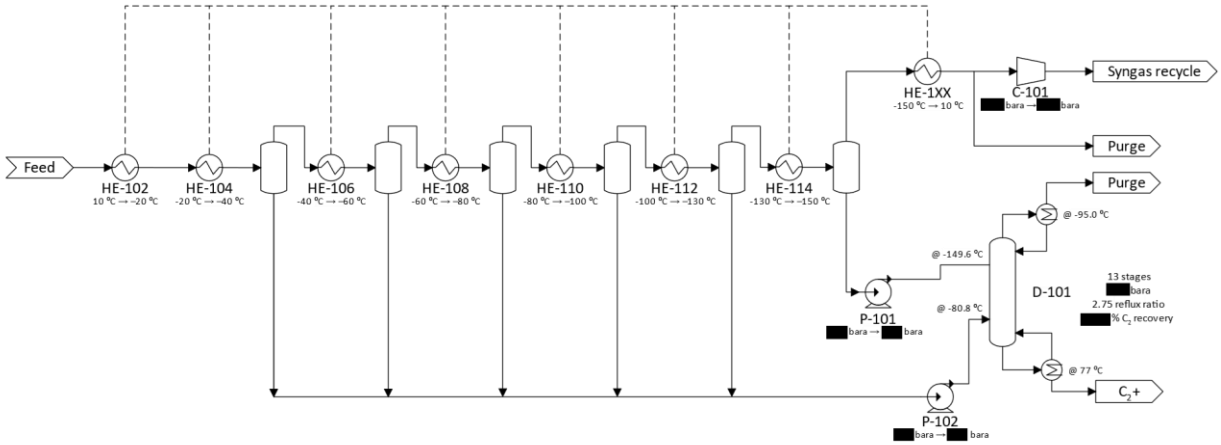

Figure 5.17. Schematic of cryogenic distillation: configuration 8.1.

This alternative is based on the configuration 6.1. In this case, the operating conditions of the column are modified to increase a condenser temperature above -100 ºC. The column has been modified to achieve similar performances to the previous configurations with the new operating conditions.

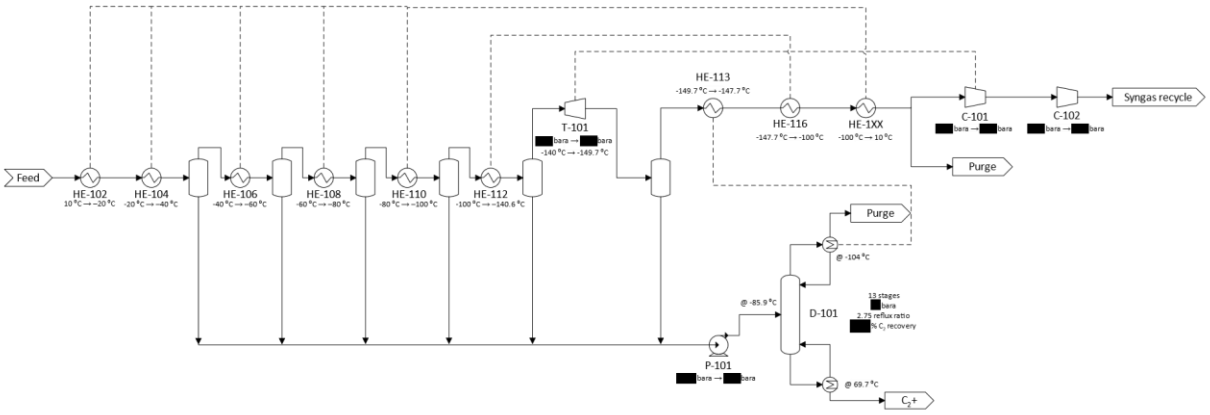

Figure 5.18. Schematic of cryogenic distillation: configuration 9.1.

This configuration does not use mixed refrigerant to achieve cryogenic temperatures, but the turbo-expansion of the syngas recycle.

In this case, *HE-112* is not using the setup described in the cooling section of Figure 5.8, as there is no refrigerant at temperatures under -100 ºC. This cooling section consists only of a heat exchanger that transfers all the energy available on the syngas recycle after the expansion until -100 ºC. By doing so, the stream is pre-cooled before the expansion on the turbine, reducing the pressure drop necessary to reach -150 ºC.

For this alternative, the condenser is operating at temperatures lower than -100 ºC and there is no mixed refrigerant available. To generate the reflux in the column (i.e., to provide cooling duty to the condenser), the syngas recycle is thermally integrated with *D-101*.

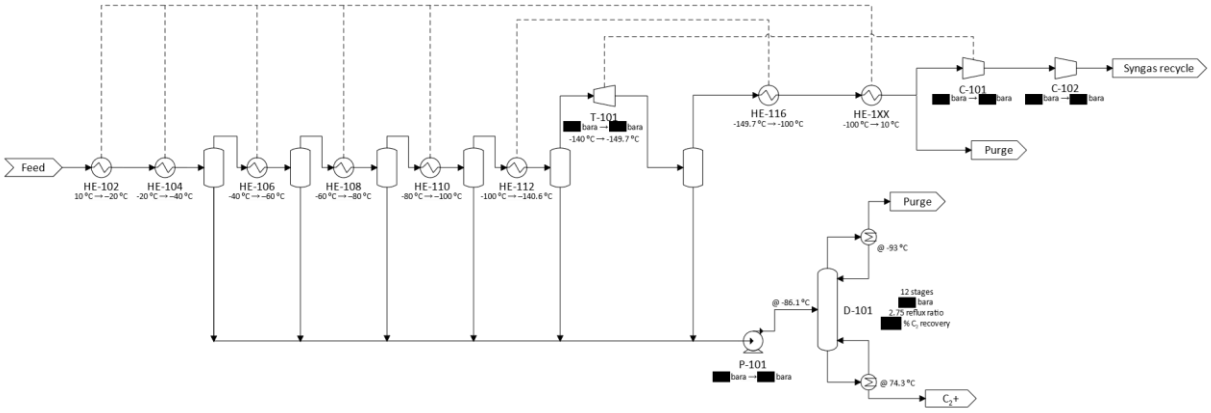

Figure 5.19. Schematic of cryogenic distillation: configuration 10.1.

This case is based on configuration 9.1. In this case, instead of using the syngas recycled to generate reflux in the column, the operation conditions of the column have been modified to be able to operate the condenser with ethylene refrigerant. The column has been modified to achieve similar performances to the previous configurations with the new operating conditions.

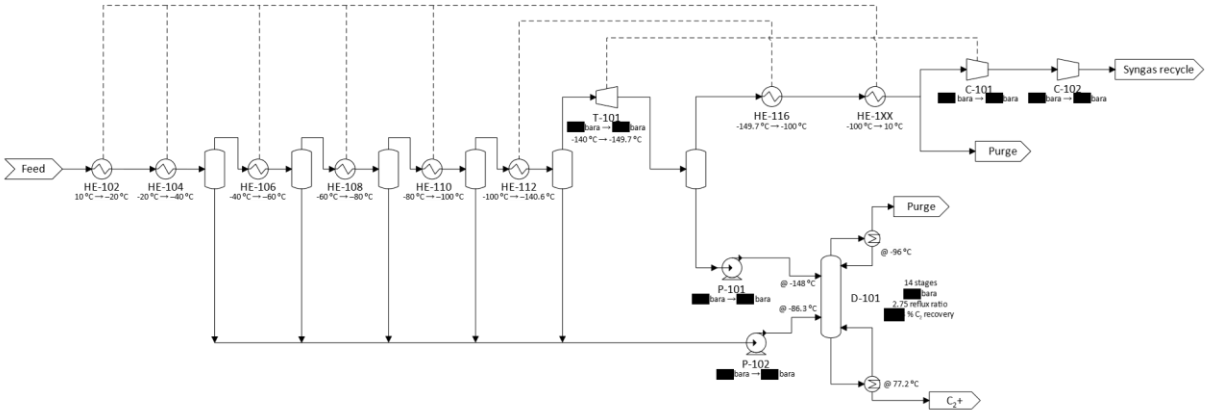

Figure 5.20. Schematic of cryogenic distillation: configuration 11.1.

This case is a combination of the configuration 6.1 (feed-splitting) with the configuration 10.1 (turbo-expansion to achieve cryogenic temperatures and operation of the column at higher temperature). The column has been modified to achieve similar performances to the previous configurations with the new operating conditions.

An economic assessment has been performed for this model to support the energy consumption study. The additional cost that the installation of a mixed-refrigerant system has been estimated by modelling a refrigeration cycle (Figure 5.21, page 46).

As the simulation of utilities and auxiliary systems is out of the scope of this project, and as the purpose of this simulation is only to estimate the magnitude of the capital cost, the refrigeration cycle is not optimized. The composition of the mixed refrigerant is of 40 $\%_{mol}$ nitrogen and 60 $\%_{mol}$ methane. The multistage compressor has been designed according to the power consumption of

cooling duty at -150 ºC obtained in the cryogenic distillation model. The CAPEX of the refrigeration cycle has only considered the cost of the multistage compressor, as it is the main contributor to the final cost.

Figure 5.21. Schematic of the refrigeration cycle simulated.

5.4.2 Extractive distillation

Property methods and solvent selection

Prediction of azeotropes using simulation software is especially dependent on the thermodynamic model chosen. For that reason, a screening of some of the most used thermodynamic models based both on equations of state and on coefficients of activity is performed to determine the method that best fits the system.

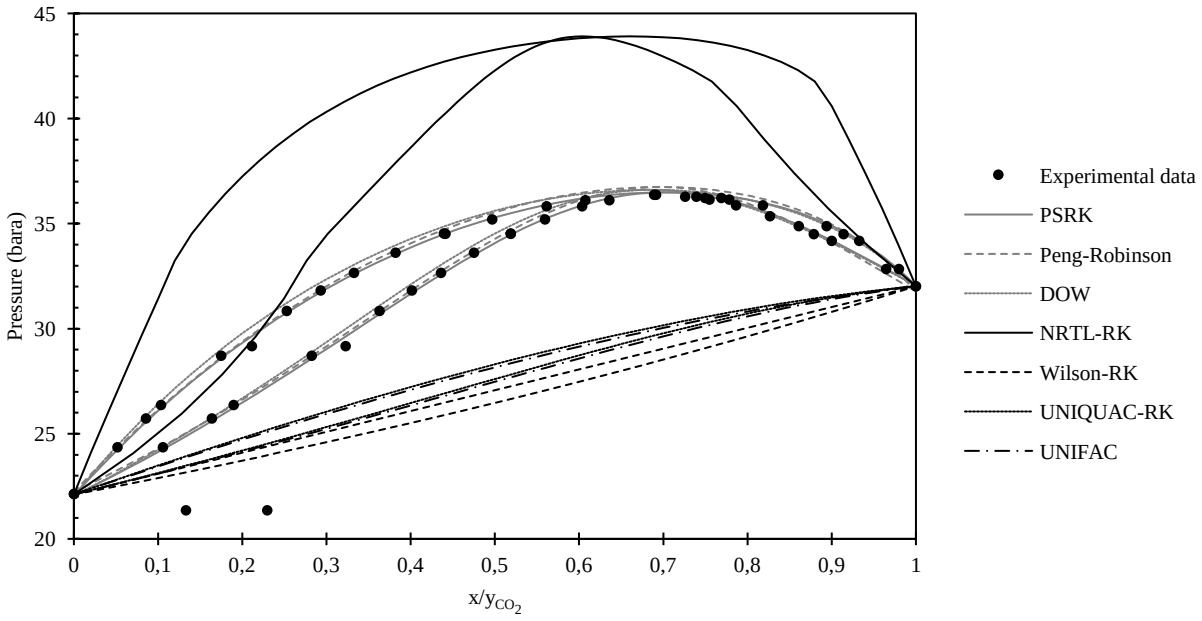

Figure 5.22. Thermodynamic model comparison for the detection of ethane-carbon dioxide azeotrope. Source of experimental data: Brown et al., 1988

Equation-of-state-based thermodynamic models are able to predict in a reliable way the position of the azeotrope and the vapor-liquid behavior of the mixture. Among all the methods, PSRK is the one that best fits the experimental data.

Coefficient-of-activity-based thermodynamic models cannot predict accurately the vapor-liquid behavior of the mixture, and only NRTL is able to predict the formation of the azeotrope in the mixture.

Given the ability to predict the azeotrope and the vapor-liquid equilibrium, PSRK is used for the solvent screening for the application of this technology. As Dow Property Method is also capable to properly predict the azeotrope and the vapor-liquid behavior of the mixture, and it is the recommended method for Dow's simulations, the technology study has been performed with this method.

Different solvents of different nature have been considered for technology. The variation of the relative volatility between CO_2 and C_2H_6 has been the chosen criteria to determine the capacity of a solvent to break the azeotrope. The results of this study can be found in *Appendix 6*. Among all the solvents assessed, pentane and methanol have been chosen due to their good performance and their frequent use in the industry.

Modelling

Two alternative designs are conceivable depending of the effect of the entrainer in the relative volatility between C_2H_6 and CO_2.

If, in the presence of the solvent, $\alpha_{CO_2,C_2H_6} > 1$; carbon dioxide is more volatile than ethane and carbon dioxide is recovered to the top of the column together with syngas and methane. All C_2+ hydrocarbons are be recovered to the bottoms. The solvent is later recovered in a regeneration column. It is the case of pentane.

If, in the presence of the solvent, $\alpha_{CO_2,C_2H_6} < 1$; ethane is more volatile than carbon dioxide, and therefore ethane is recovered to the top of the column together with syngas and methane. While all C_3+ hydrocarbons and CO_2 are recovered to the bottoms. Further separation units are required as C_2 must be separated from syngas and CO_2 must be recovered from the hydrocarbons stream. It is the case of methanol. Two designs are possible according to the operation of the extractive distillation column:

- Low recovery of C_2H_6 to the top, but very few CO_2 is recovered together with the ethane.
- High recovery of C_2H_6 to the top, but many CO_2 is recovered together with the ethane.

Figures 5.23 and 5.24 (page 48) show a schematic of the mentioned distillation strategies.

Technologies to recover carbon dioxide can be any of the ones already described in *4.3. CO2 recovery*, or it can be a simple distillation column at the cost of losing some C_2.

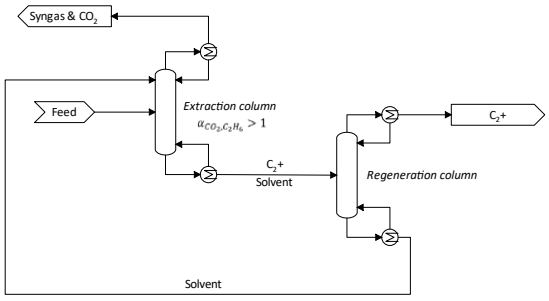

Figure 5.23. Extractive distillation strategy for $\alpha_{CO2,C2H6} > 1$.

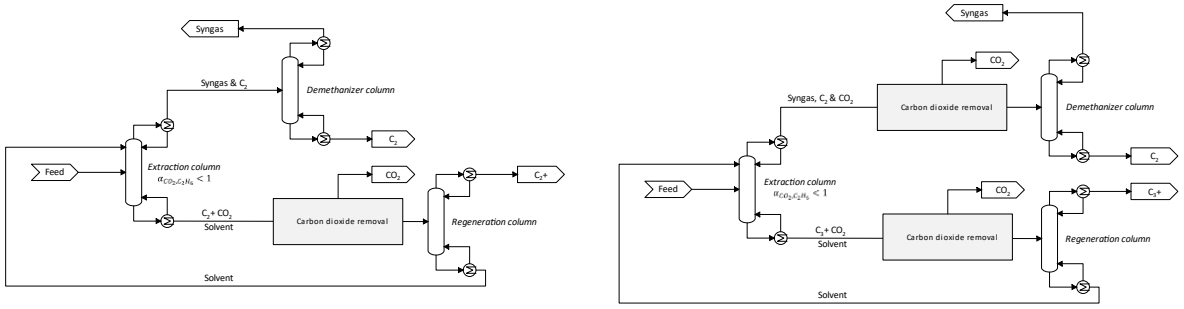

Figure 5.24. Extractive distillation strategies for $\alpha_{CO2,C2H6} < 1$ with low (left) and high (right) recovery of C_2 in the extraction column.

As already explained in *5.1. Software modelling with Aspen Plus*, the thermodynamic property methods used in the models have been customized based on Dow internal research and operational expertise. However, the thermodynamic property method used for the extractive distillation column for pentane is PSRK, as Dow´s internal method is not customized for azeotropic distillation.

A total of 5 configurations have been analyzed to select the option with the lowest energy consumption. Figures from 5.25 to 5.29 (pages 49, 50, 52, 53 and 54) illustrate the models developed for extractive distillation. Guidelines to understand the figure and the model are:

- Unit HE-1XX represents a series of exchangers.
- The amine wash and the multistage compressor *C-103* are not detailed in this model. A more developed model for this unit operation is found in *5.3.1. Amine washes*.
- Solvent make-up is not drawn in the figures but calculated in the model.

Sublimation temperature of carbon dioxide is an important parameter to consider. Pure carbon dioxide sublimates at temperatures between -65 and -85 °C; but there is few experimental data in the literature describing the sublimation temperature of CO_2 in a mixture. In the described processes, sublimation may only occur in the condenser of extractive distillation columns (as in other regions of the process the temperatures are higher, or the concentration of carbon dioxide is too low). Given the uncertainty of the sublimation temperature of CO_2 in a mixture, and that the study only aims the scenarios with the lowest energy consumption for comparison reasons, carbon dioxide has been assumed not to sublimate at the studied temperatures (down to -115 °C).

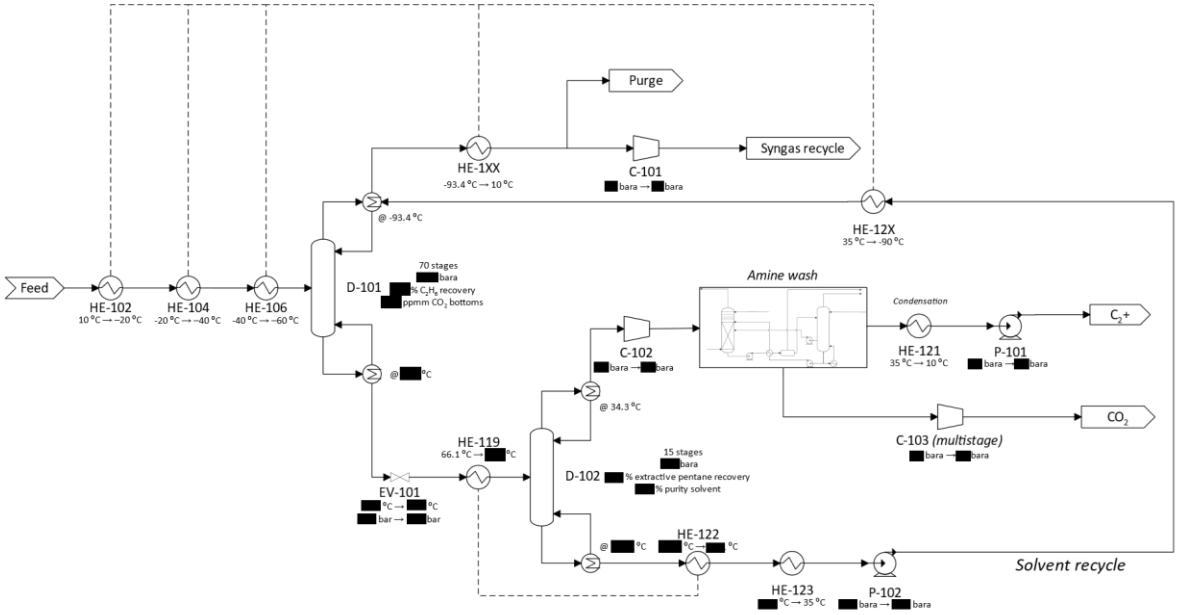

Figure 5.25. Model for extractive distillation using pentane as solvent.

The feed stream is cooled down and fed to the extractive distillation column. The objective of this reduction of temperature is to reduce the condenser duty, as it is operating at low temperatures.

Some design decisions taken when modelling the extractive distillation column *D-101* are:

- An operating pressure close to the inlet pressure is chosen to avoid non-isobaric processes that would significantly increase the energy consumption. Lower pressures can reduce the energy consumption of the column but would further decrease the temperature of the condenser.
- Stage number is selected for optimization of energy by reducing the reflux ratio. The column is not used in sizing estimates for CAPEX.
- The gaseous feed stage has been chosen to favor the separation and avoid potential hydrodynamic problems. Solvent is fed to the condenser to create an entrainer-rich reflux: as the entrainer is a heavy compound, it is the only option to have a high concentration of it in the condenser.
- A partial-vapor condenser is selected, as the distillate has a high concentration of incondensable substances.

Design specifications provide a minimum recovery of ethane to the bottom of the column of [redacted] % and a maximum concentration of carbon dioxide to the bottom of [redacted] ppmm.

The solvent flowrate is chosen to minimize the overall energy consumption of the system while still allowing a good separation. The purity of the solvent pentane is of [redacted] % (the rest is n-butane).

The distillate of *D-101* (syngas, methane and CO_2) is heated, compressed and sent back to the reactor. This recycle uses part of its energy to pre-cool the stream fed to the column.

The stream obtained to the bottom of *D-101* (solvent and C_2+) is depressurized to the operating pressure of *D-102* and fed to it.

Some design decisions taken when modelling the column *D-102* are:

- Operating pressure is reduced to decrease the energy consumption as much as possible while avoiding condenser temperatures lower than 35 – 40 °C. Lower temperatures would not allow the use of cooling water to provide cooling duty to the condenser.
- Stage number is selected for optimization of energy by reducing the reflux ratio. The column is not used in sizing estimates for CAPEX.
- A partial-vapor condenser is selected, as the amine wash feed is preferably vapor.

Design specifications provide a recovery of solvent of [redacted] % and a purity of [redacted] $\%_{mol}$.

The distillate of *D-102* is re-compressed to the operating pressure of the amine wash. After CO_2 recovery, the stream obtained is the main product (C_2+).

The regenerated solvent obtained to the bottom of *D-102* is cooled down and used to pre-heat the feed of the column. By doing so, the reboiler duty of the column decreases, reducing the energy consumption. The entrainer is re-pressurized to the operating pressure of *D-101* and cooled down to the condenser temperature of the extractive distillation column using the syngas recycle.

As described in *2.2. Basis of engineering*, methane and nitrogen must be purged to prevent build-up. Both purges have been located at the streams where the ratio of the component to be purged relative to the components that are not desired to purge is the highest.

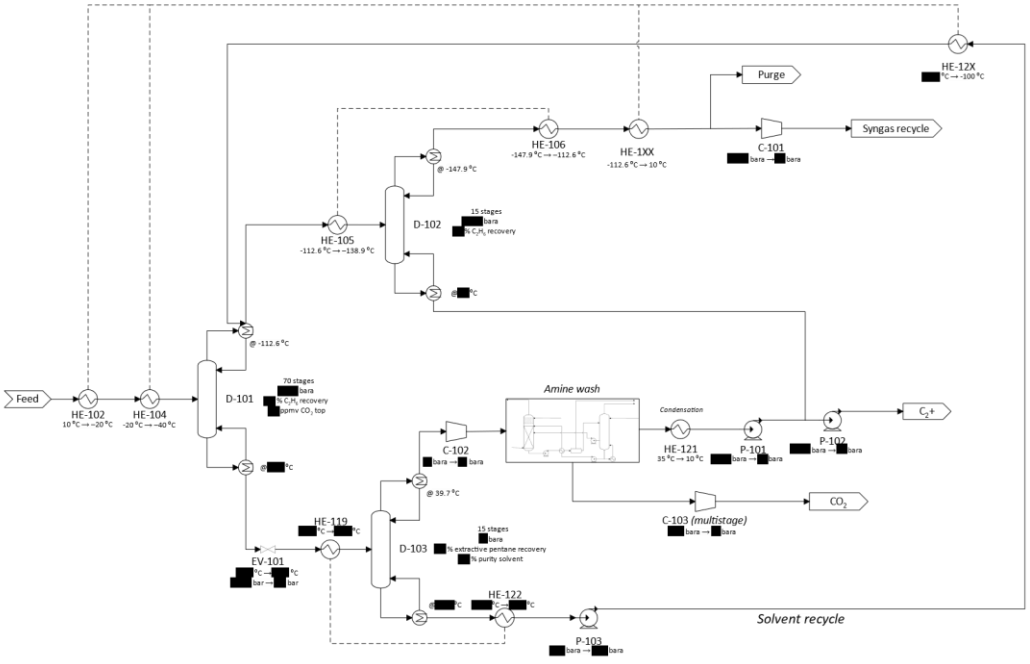

Figure 5.26. Model for extractive distillation using methanol as solvent.
Case with high recovery of ethane to the top of D-101 and use of amine wash to recover CO_2.

The feed stream is cooled down and fed to the extractive distillation column. The same design choices already described for pentane *D-101* (page 49) apply to this model.

Design specifications provide a minimum recovery of ethane to the top of the column of [redacted] % and a maximum concentration of carbon dioxide to the top of [redacted] ppmv.

The solvent flowrate is chosen to minimize the overall energy consumption of the system while still allowing a good separation. The purity of the solvent methanol is of [redacted] %.

The stream obtained to the bottom of *D-101* (solvent, CO_2 and C_3+) is depressurized to the operating pressure of *D-103* and fed to it. The same design choices already described for pentane *D-102* (page 50) apply to this model.

Design specifications provide a recovery of solvent to the bottom of [redacted] % and a purity of [redacted] $\%_{mol}$.

The distillate of *D-103* is re-compressed to the operating pressure of the amine wash. After CO_2 recovery, the stream obtained is one of the main products (C_3+).

The regenerated solvent obtained to the bottom of *D-103* is cooled down and used to pre-heat the feed of the regeneration column. The entrainer is re-pressurized to the operating pressure of *D-101* and cooled down to the condenser temperature of the extractive distillation column using the syngas recycle.

The distillate of *D-101* (syngas, methane and C_2) is cooled down and sent to the demethanizer (*D-102*). Some design decisions taken when modelling the column are:

- Operating pressure is close to the inlet pressure to avoid non-isobaric processes. Low pressures are usually used to decrease the energy consumption of a distillation column, but in this case decreasing the pressure would lead to a decrease of temperature below -150 °C.
- Stage number is selected for optimization of energy by reducing the reflux ratio. The column is not used in sizing estimates for CAPEX. If the alternative is further studied, stage number must be modified to achieve a balance between the energy consumption and the capital costs.
- A partial-vapor condenser is selected, as the distillate has a high concentration of incondensable substances.

Design specifications provide a recovery of ethane to the bottom of [redacted] % and minimize the energy consumption of the reboiler while aiming condenser temperatures higher than -150 °C and enough reflux for a proper operation.

The distillate of *D-102* (syngas and methane) is heated, compressed and sent back to the reactor. This recycle uses part of its energy to pre-cool the stream fed to columns *D-101* and *D-102* with the objective of reducing the condenser duty of the columns.

The stream obtained to the bottom of *D-102* is re-compressed and obtained as one of the main products (C_2+).

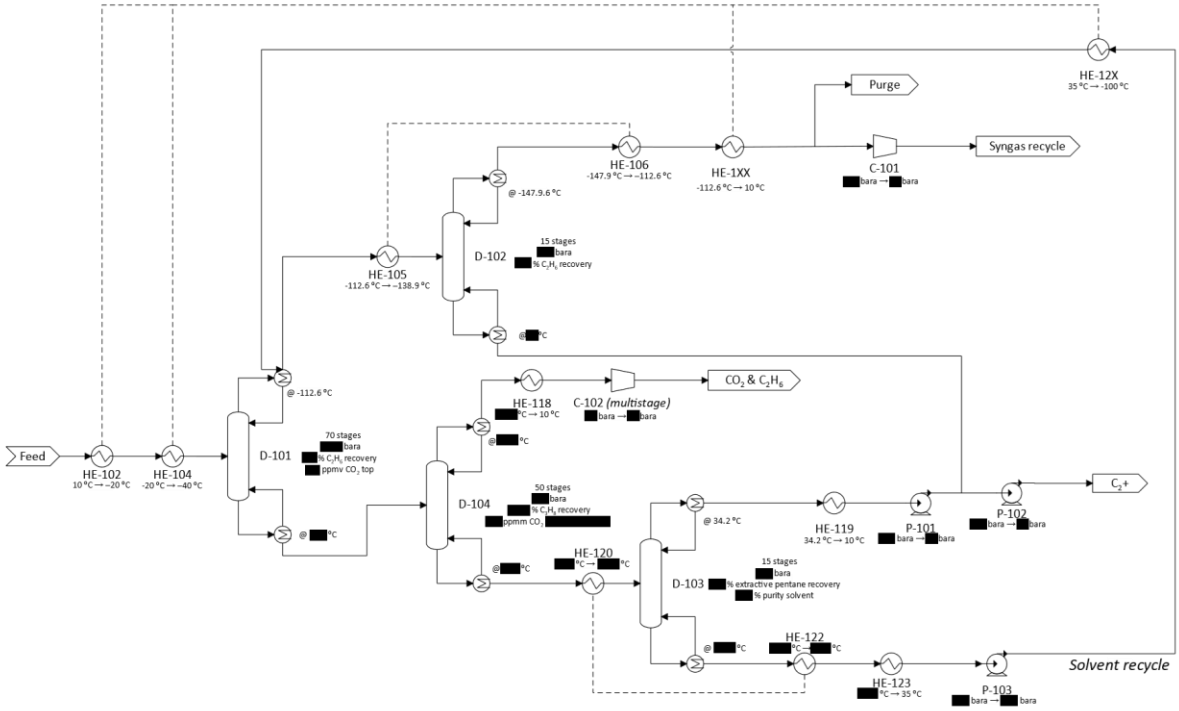

Figure 5.27. Model for extractive distillation using methanol as solvent. Case with high recovery of ethane to the top of D-101 and use of distillation to recover CO_2.

The feed stream is cooled down and fed to the extractive distillation column. The same design choices already described for methanol *D-101* (page 51) apply to this model.

The distillate of *D-101* (syngas, methane and C_2) is cooled down and sent to the demethanizer. The same design choices already described for methanol *D-102* (page 51) apply to this model.

The distillate of *D-102* (syngas and methane) is heated, compressed and sent back to the reactor. This recycle uses part of its energy to pre-cool the stream fed to columns *D-101* and *D-102* with the objective of reducing the condenser duty of the columns. The stream obtained to the bottom of *D-102* is re-compressed and obtained as one of the main products (C_2+).

The stream obtained to the bottom of *D-101* (solvent, CO_2 and C_3+) is depressurized to the operating pressure of *D-104* and fed to it. Design decisions taken when modelling *D-104* are:

- Operating pressure: the pressure is reduced to decrease the energy consumption of the column. Pressure has been reduced as much as possible without achieving too low condenser temperatures. Although re-compression energy increases when operating the column at lower pressures, the re-compression costs are lower than the cost of operating the column at a higher pressure.
- Stage number is selected for optimization of energy by reducing the reflux ratio. The column is not used in sizing estimates for CAPEX.
- A partial-vapor condenser is selected, as the distillate has a high concentration of CO_2.

Design specifications provide a recovery of propane to the bottom of [redacted] $\%_{mol}$ and a concentration of [redacted] ppmm of CO_2 in the final product.

The distillate of *D-104* is a mixture of carbon dioxide and ethane (few C_2 are lost as *D-101* is recovering most part of them).

The bottoms of the column is sent to *D-103*. The same design choices already described for pentane *D-102* (page 50) apply to this model for *D-103*, with the exception of the type of condenser. As CO_2 has already been removed in the extractive distillation column, there is no need for the distillate to be in gaseous state, so a total condenser is used. The distillate of *D-103* is one of the main products (C_3+).

The regenerated solvent obtained to the bottom of *D-103* is cooled down, repressurized and sent back to *D-101*.

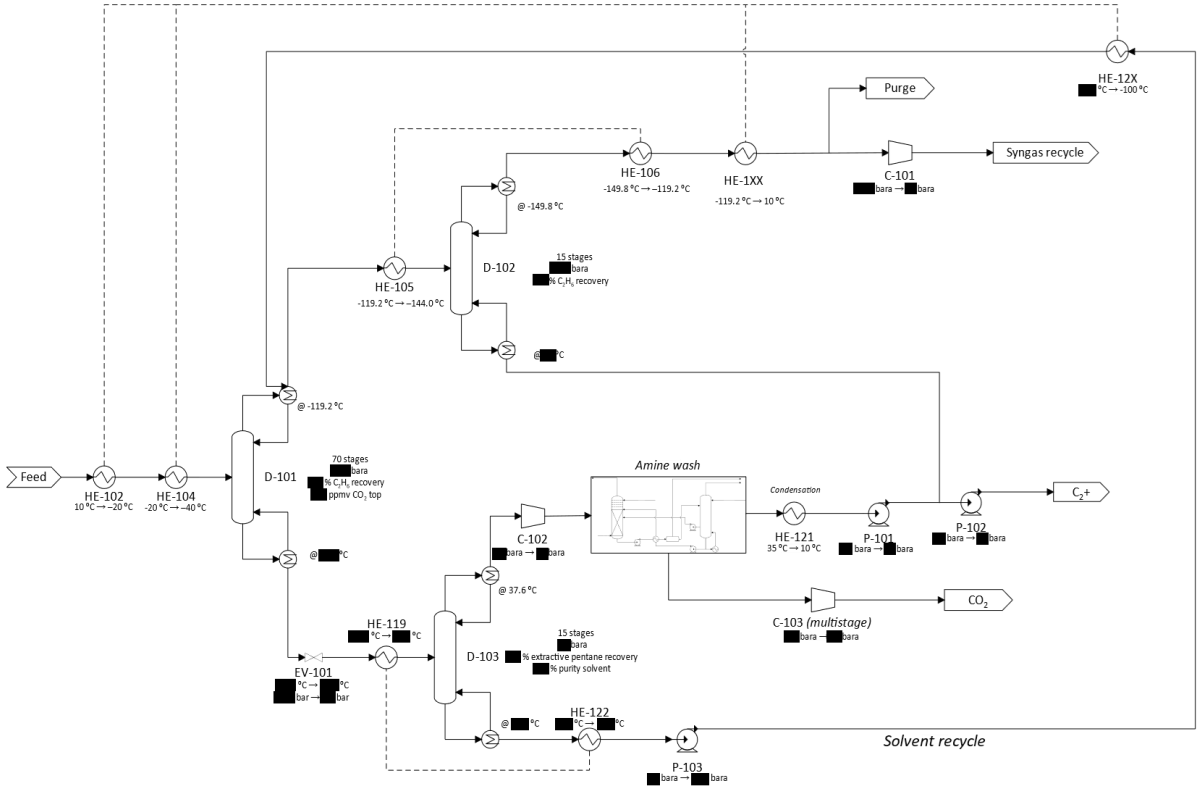

Figure 5.28. Model for extractive distillation using methanol as solvent.
Case with low recovery of ethane to the top of D-101 and use of amine wash to recover CO_2.

The description of the model is the same than that of Figure 5.26. The main difference with that model is that, in this model, *D-101* design specifications provide a minimum recovery of ethane to the top of the column of [redacted] % and a maximum concentration of carbon dioxide to the top of [redacted] ppmv.

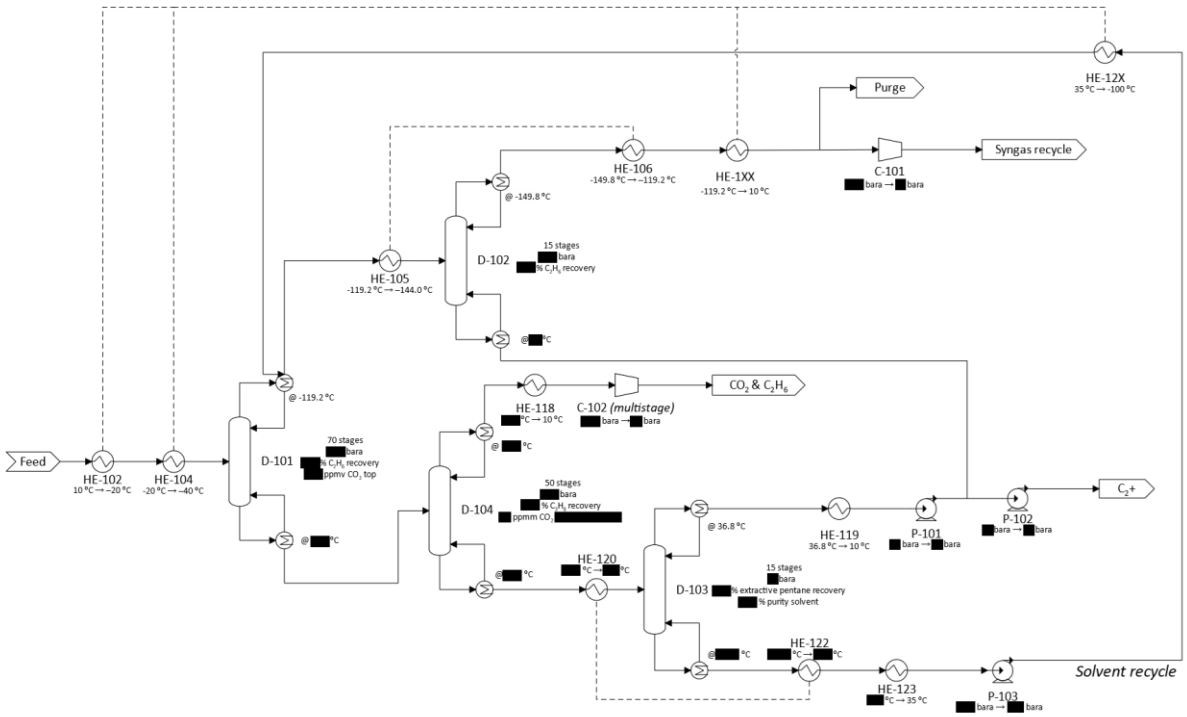

Figure 5.29. Model for extractive distillation using methanol as solvent. Case with low recovery of ethane to the top of D-101 and use of distillation to recover CO_2.

The description of the model is the same than that describing Figure 5.27. The main differences with that model are:

- *D-101* design specifications provide a minimum recovery of ethane to the top of the column of [redacted] % and a maximum concentration of carbon dioxide to the top of [redacted] ppmv.

- Distillate of *D-104* is still a mixture of carbon dioxide and ethane, but as *D-101* is not recovering anymore most part of it, high amounts of C_2 are lost.

5.4.3 Pressure swing distillation

Vapor-liquid equilibrium (pressure selection)

A *Txy* diagram at different pressures for the binary mixture CO_2-C_2H_6 has been elaborated using Dow internal thermodynamic property methods with the objective to have a better understanding of the sensitivity of the azeotrope to pressure and to find the two column operating pressures.

Figure 5.30 (page 55) shows that large pressure differentials only cause slight differences in the azeotrope, anticipating a challenging operation.

The operating pressures used for the model are the inlet pressure for the high-pressure column and [redacted] bara for the low-pressure column.

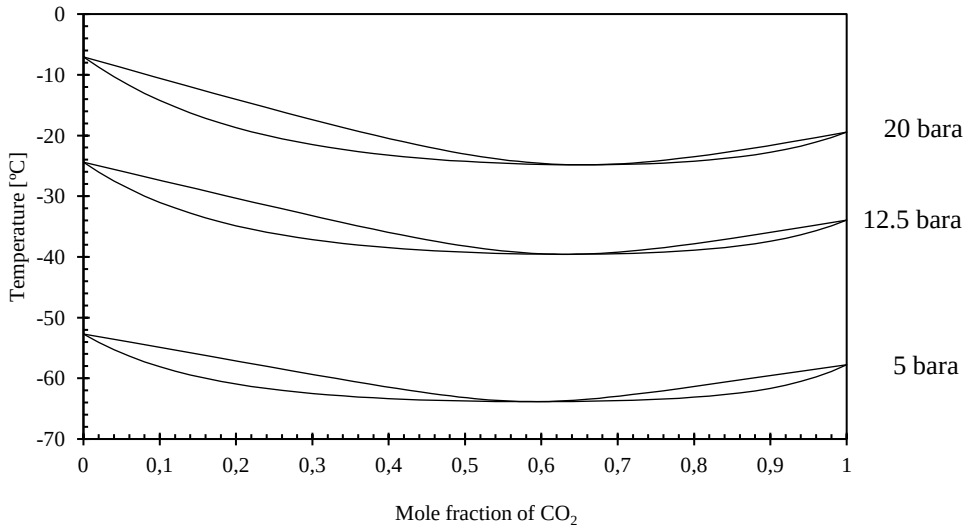

Figure 5.30. Txy diagram for different pressures of the mixture CO_2-C_2H_6 using Dow's internal thermodynamic database (pressures above 20 bara are not shown).

Binary separation

The binary system CO_2-C_2H_6 has been studied to have a better understanding of the technology. Figure 5.31 illustrates the model developed. The dry feed is fed to the high-pressure distillation column.

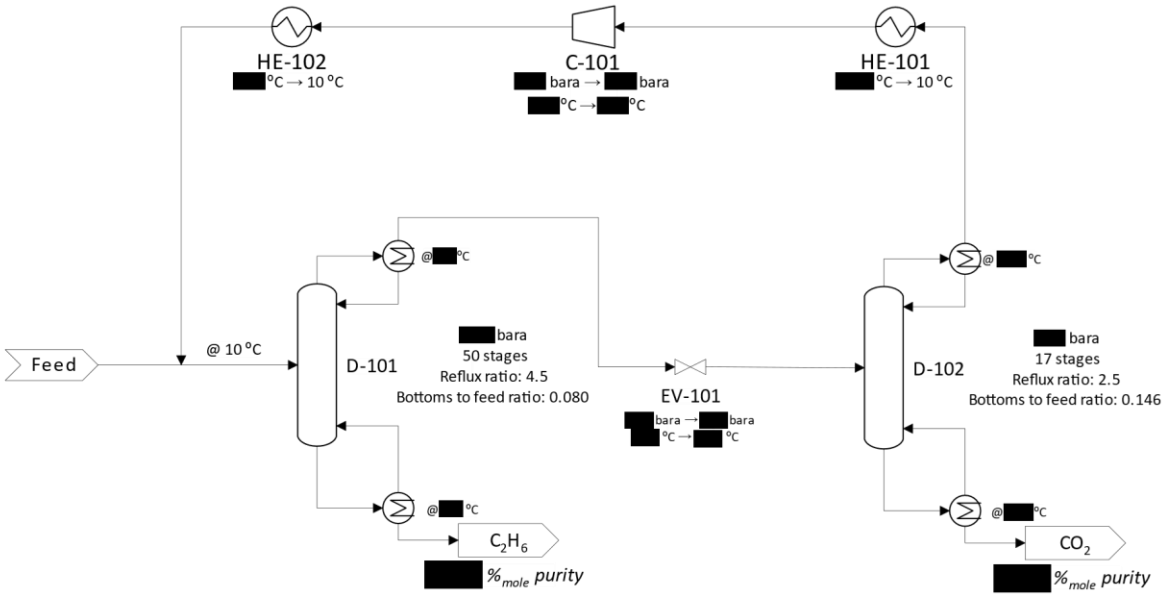

Figure 5.31. Schematic of the binary pressure swing distillation system.

Some design decisions taken when modelling the high-pressure distillation column are:

- An operating pressure close to the inlet pressure is chosen to avoid non-isobaric processes.
- Stage number is selected for optimization of energy by reducing the reflux ratio. The column is not used in sizing estimates for CAPEX.
- A total condenser is selected, as the distillate has a high concentration of CO_2.

Design specifications provide a purity of ethane to the bottom of the column of [redacted] $\%_{mol}$ while trying to minimize the energy consumption of the column.

The distillate of *D-101* (CO_2-C_2H_6 at the azeotropic composition) is de-compressed and sent to the low-pressure distillation column. Except for its pressure, similar design decisions to *D-101* are taken for *D-102*. The bottom stream is pure ethane.

Design specifications provide a purity of carbon dioxide to the bottom of the column of [redacted] $\%_{mol}$ while trying to minimize the energy consumption of the column.

The distillate of *D-102* (CO_2-C_2H_6 at the azeotropic composition) is re-compressed and sent to the high-pressure distillation column. The bottom stream is pure carbon dioxide.

The following observations can be extracted from the results:

- A high-pressure column with a very large number of theoretical stages is needed because the feed composition is very close to the azeotropic one.
- Given the low sensitivity of the azeotrope to pressure and that the feed composition is very close to the azeotropic one, a very high recirculation is needed to achieve high purity product.

Reactor outlet mixture separation (previous dehydration)

Several challenges were found when modelling the system:

- Very low product flowrates are obtained given the low sensitivity of the azeotrope to pressure and the feed composition close to the azeotropic one.
- Very low temperatues achieved in the condenser of the high-pressure distillation column and the low-pressure distillation column, potentially far below the sublimation point of carbon dioxide.
- The large internal recycle between the low-pressure column distillate and the high-pressure column feed is also containing the unreacted syngas. Additional separation units have to be integrated to recover C_2 and CO_2 from the uncondensable gases to allow the external recycle of syngas.

Given the drawbacks that the use of this technology implies, it has been decided to explore other technologies that better fit the characteristics of the process.

Therefore use of this technology is dismissed and will undergo any further evaulation or assessment.

6 RESULTS AND DISCUSSION

6.1 Water removal

6.1.1 Energy consumption analysis

The results for the energy consumption analysis for the different dehydration technologies assessed are illustrated in Figure 6.1.

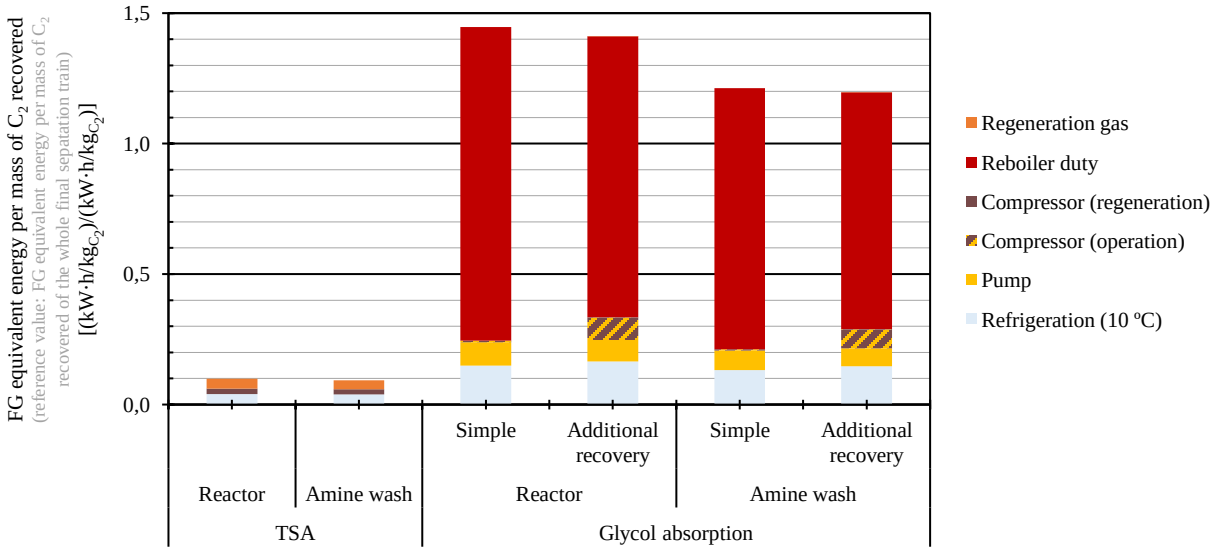

Figure 6.1. Normalized fuel power consumption for the different alternatives for dehydration. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The analysis shows that the energy consumption of glycol dehydration is significantly higher than that of TSA dehydration at the working conditions of the process.

Some of the main outcomes that can be extracted from the models developed are:

- Cooling energy consumption is higher for glycol absorption. In addition to the energy required to reduce the temperature of the feed to 10 °C (necessary for both technologies), absorption requires additional refrigeration of the solvent to improve its efficiency.
- Heating energy consumption is higher for glycol absorption. For TSA, it is reduced to the heat needed to raise the temperature of the regeneration gas up to 235 °C to improve the desorption of water from the catalyst. For physical absorption, reboiler duty consumes most part of the energy, as it must heat all the solvent, partially evaporate it, and boil the water. Lower molecular weight solvents may reduce reboiler duty.
- Compression energy is dependent of the configuration of the process. For glycol absorption without additional recovery, it is low, as compressors are only used to re-compress the vapors of a partially de-compressed stream. For TSA, it is higher, as it must increase the pressure of the regeneration gas to operation conditions. For glycol absorption with additional recovery, it is very high, as it must re-compress all the gas obtained from the regeneration of the solvent at 1 bara.

- Pumping energy is used only for glycol absorption, as solvent must be re-pressurized after regeneration. Processes using solvents usually dedicate a significant fraction of their power consumption to pump or re-pressurize the solvent.
- Energy consumption to dehydrate feeds coming from the amine wash is lower than that to dehydrate feeds coming directly from the reactor. Although chemical absorption saturates the gas with water, absence of CO_2 in the stream modifies the vapor-liquid equilibrium and increases the efficiency of condensation of water in *HE-101*. As less water is being fed to the system, the energy consumption is lower.
- Scenarios where glycol absorption uses additional recovery consume less energy per mass of C_2 recovered. Although the total non-normalized energy consumption is higher, the normalized value is lower because the recovery is also significantly higher.

Other learnings extracted from the models developed are found in *Appendix 7*, where a more detailed analysis of the results is found.

Results show large amounts of C_2+ absorbed by the glycol and lost in the process. The recovery of hydrocarbons during the dehydration process without additional recovery is presented in Table 6.1. No product is lost in designs with additional recovery.

Table 6.1. Hydrocarbon recovery for the different glycol dehydration scenarios without additional recovery.

Species	Feed from reactor	Feed from amine wash
CH_4	99.4 %	99.5 %
C_2	89.6%	90.7%
C_3	43.3%	49.7%
C_4	2.4%	2.2%
C_5	0.9%	0.8%
Total	56.3%	59.9%

6.1.2 Sensitivity analysis of the concentration of water in the dry gas

A sensitivity analysis has been carried out to further understand the potential of the technologies explored. The results of this study are relevant to the decision of which technology is most suitable and are, therefore, summarized below. A more detailed analysis of the results is found in *Appendix 8*.

For the study, different water concentrations in the dry gas have been aimed in TSA and glycol absorption. Regeneration and solvent flowrate, respectively, have been modified to achieve the new specifications. The energy consumption in function of the concentration of water in the dry gas is found in Figure 6.2. The recovery of hydrocarbons in the same conditions is found in Figure 6.3.

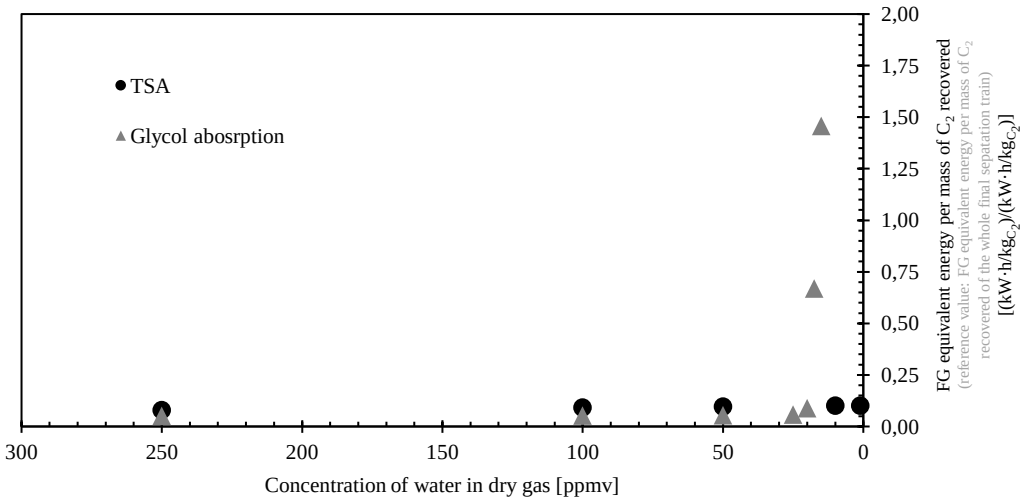

Figure 6.2. Fuel power consumption comparison for the dehydration sensitivity analysis. ***Results have been normalized to the energy consumption of the final primary separation unit.***

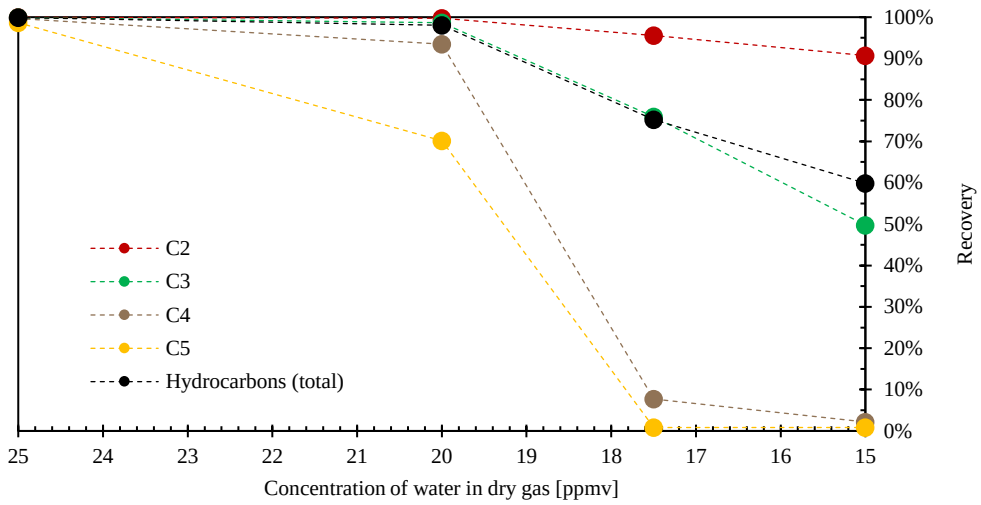

Figure 6.3. Hydrocarbon losses for glycol dehydration (sensitivity analysis)

The main outcomes derived from the sensitivity analysis are:

- TSA follows a linear energy increment over the concentration of water aimed in the dry gas. Glycol absorption follows an exponential-like increment.
- The energy consumption of glycol absorption is lower than that of TSA when aiming concentrations of water in the dry gas higher than 20 ppmv. For concentrations below this value, glycol absorption is significantly more energy-consuming than TSA.
- The recovery of hydrocarbons in glycol absorption is almost 100 % when aiming concentrations of water in the dry gas higher than 25 ppmv. When lower concentrations are aimed, the recovery steeply drops.

Both operations perform similarly in terms of energy consumption and hydrocarbon recovery when aiming concentrations of water in the dry gas down to 25-20 ppmv. From this point on, the energy consumption of glycol absorption increases exponentially-like.

This behavior is described with Henry's law. For a given concentration of water in the lean solvent, there is a minimum partial pressure of water in the gas. To further reduce the concentration of water in the gas, the fraction of water in the liquid must decrease. To do so, the solvent flowrate must increase to reduce the concentration of water in the liquid phase even considering the increased absorption of water in the solvent.

6.1.3 Best alternative

The analysis shows that the energy consumption of glycol dehydration is significantly higher than that of TSA dehydration at the working conditions of the process.

Process optimization (solvent selection analysis, redesign of the regeneration column, etc.) could decrease the overall energy consumption of glycol dehydration, but the sensitivity analysis shows that its consumption when aiming near-subppm concentrations is excessive. As a consequence, the utilization of this technology within this particular context becomes unfeasible.

An additional challenge arises from the loss of hydrocarbons in the process (especially long-chain molecules). To mitigate this issue, supplementary equipment is required to recover the absorbed hydrocarbons. This, in turn, leads to a further increased energy consumption and system complexity.

On the other hand, molecular sieve dehydration is robust and simple, two must-have characteristics of process critical operations.

Therefore, TSA is the chosen option for the process if the installation of only one technology is possible.

Some of the challenges mentioned for glycol absorption can be solved by combining both technologies. Glycol dehydration can be used for bulk water removal down to approximately 25 ppmv (still low energy consumption, and almost negligible hydrocarbon losses) and TSA can be used for refining. Although some challenges inherent to glycol absorption would still have to be addressed, the overall energy consumption would decrease, and no hydrocarbons would be lost in the process.

Further study to determine the feasibility of the combination of both technologies is out of the scope of this project, but it should be taken into consideration during subsequent project assessments.

6.2 CO_2 recovery

6.2.1 Sensitivity analysis of the temperature in the absorption column for Rectisol® technology

The results for the sensitivity analysis to determine the best feed and solvent temperatures of the gas in the absorption are illustrated in Figure 6.4.

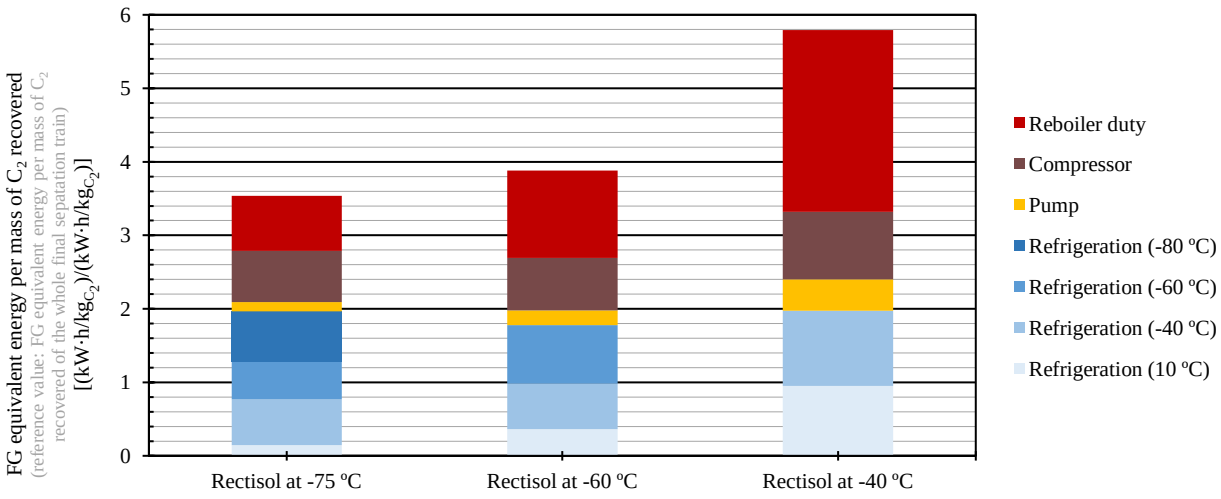

Figure 6.4. Normalized fuel power consumption for different gas feed and solvent temperatures in the absorption column for Rectisol®. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The analysis shows that the energy consumption of Rectisol® technology increases with temperature in the studied process.

Some of the main outcomes that can be extracted from the models developed are:

- Reboiler energy consumption decreases with temperature. The lower the temperature, the better the absorption of CO_2 in the solvent and the lower the solvent flowrate needed to achieve process specifications.
- Cooling energy consumption has a minimum at -60 °C. When considering only cooling duty, the same reasoning as for the reboiler energy consumption is followed. However, dissipating heat at lower temperatures requires a high electrical power. When combining both mechanisms, a minimum is found at an intermediate temperature.
- Pumping energy consumption increases with temperature. The higher the temperature, the worse the absorption of CO_2 in the solvent and the higher the solvent flowrate needed to achieve process specifications. This is translated into a higher pumping energy.

Other learnings extracted from the models developed are found in *Appendix 9*, where a more detailed analysis of the results is found. Additional information about the recovery of hydrocarbons at the different temperatures studied is also found in the referenced appendix.

Based on the results obtained, the gaseous and the solvent feed temperatures of the absorption column are -75 °C. Although this temperature is close to the sublimation point of CO_2, it is not expected to find carbon dioxide that is not dissolved in TEG at this temperature in the absorption column. Special attention has to be paid to the gaseous feed of the column, as some of the feed condensates at this range of temperatures and the concentration of CO_2 in the condensate is relatively high. As the objective of the analysis is to have a better understanding of the technology at its best performance conditions, the study is performed at this temperature for comparison reasons.

6.2.2 Energy consumption analysis

The results for the energy consumption analysis for the different carbon dioxide recovery technologies assessed are illustrated in Figure 6.5.

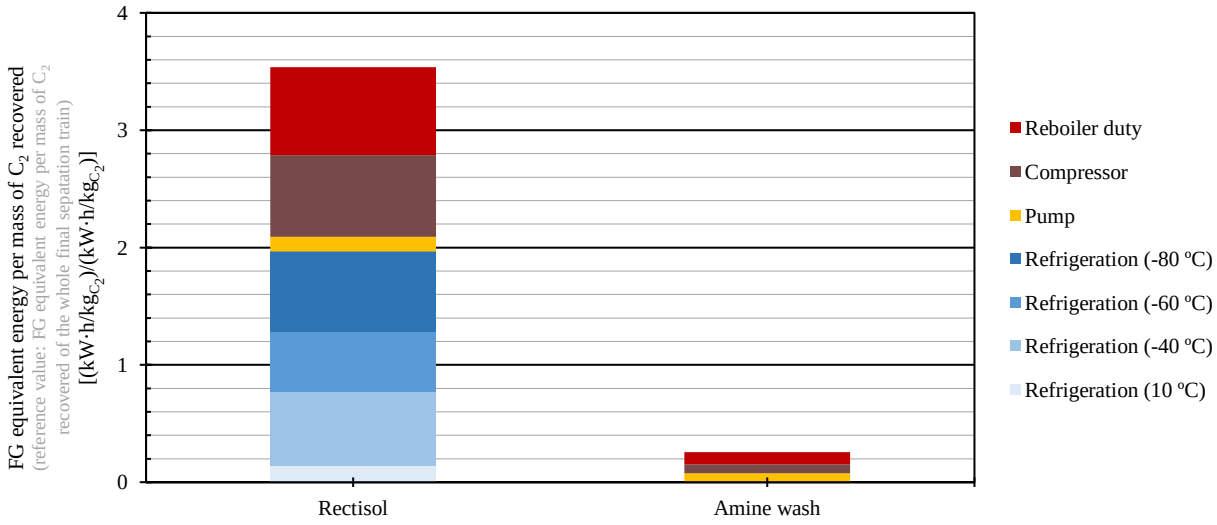

Figure 6.5. Normalized fuel power consumption for the different alternatives for CO_2 recovery. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The energy consumption analysis shows that the energy consumption of Rectisol® process is significantly higher than amine wash CO_2 recovery at the working conditions of the process.

Some of the main outcomes that can be extracted from the models developed are:

- Cooling energy is only assessed for Rectisol®. Although amine washes may use some cooling water to refrigerate water condensate, the energetic consumption is negligible when compared to Rectisol®. This technology requires the use of a large flowrate of methanol at low temperatures that leads to a high cooling energy consumption (more than 50 % of the total energy consumption).
- Heating energy consumption is also higher for Rectisol®. Like for glycol dehydration, physical absorption methods significantly increase their energy consumption when aiming low concentrations of CO_2 (see *Appendix 11*). Additionally, the model used for amine wash uses partial regeneration of the solvent to reduce the reboiler duty of the regeneration column, further increasing the difference in heat energy consumption in both alternatives.
- Compression energy is significantly higher for Rectisol®. Although both technologies must re-compress CO_2 from approximately 1 bara to high pressure, Rectisol® has a low recovery of hydrocarbons. These end up in the distillate of the regeneration column and are compressed together with the carbon dioxide, leading to a substantial rise in compression energy.
- Pumping energy is of the same order of magnitude for both technologies.

- High power consumption of pumping and regeneration in the amine wash is explained by the low partial pressure of CO_2 at the feed. As solvent is only partially regenerated and acts as physical absorbent, partial pressure of CO_2 is the main driving force for absorption. This low concentration of CO_2 decreases absorption, increasing solvent flowrate and, therefore, power consumption of the technology. Higher pressures or higher concentrations of CO_2 would enhance the performance of the unit (at a cost of higher re-compression energy).

Other learnings extracted from the models developed are found in in *Appendix 10*, where a more detailed analysis of the results is found.

Results show large amounts of hydrocarbons absorbed by methanol in Rectisol® and lost in the process. The recovery of hydrocarbons during the CO_2 recovery process is presented in Table 6.2.

Table 6.2. Hydrocarbon recovery for Rectisol® at -75 °C

Species	Recovery [%]
CH_4	93.1
C_2	34.1
C_3	0.02
C_4	1.15
C_5	0.94
C_2+	13.3

6.2.3 Sensitivity analysis of the CO_2 removal capacity

A sensitivity analysis has been carried out to understand the potential of Rectisol® technology and compare it to amine washes. A more detailed analysis of the results is found in *Appendix 11*.

For the study, different carbon dioxide concentrations in the treated gas have been aimed for Rectisol®. Solvent flowrate has been modified to achieve the new specifications. Energy consumption in function of the concentration of CO_2 in the treated gas is found in Figure 6.6, while recovery of hydrocarbons in the same conditions is found in Figure 6.7.

The main outcomes derived from the sensitivity analysis are:

- Rectisol® follows an exponential-like increment. This behavior is already described in *6.1.2. Sensitivity analysis of the concentration of water in the dry gas*.
- The energy consumption of Rectisol® is always higher than the energy consumption of amine wash to achieve near-subppm concentrations of CO_2.
- The recovery of hydrocarbons in Rectisol® is always low in the studied range of aimed CO_2 concentrations in the treated gas.

Amine wash is best performing in terms of energy consumption and hydrocarbon recovery in the whole range of aimed CO_2 concentrations in the treated gas that has been studied.

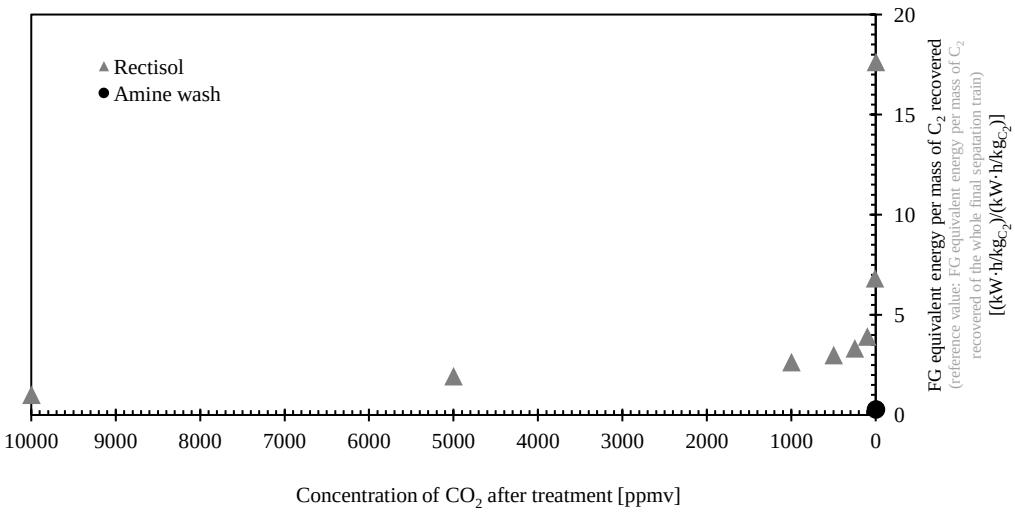

Figure 6.6. Normalized fuel power consumption for the CO_2 recovery sensitivity analysis. ***Results have been normalized to the energy consumption of the final primary separation unit.***

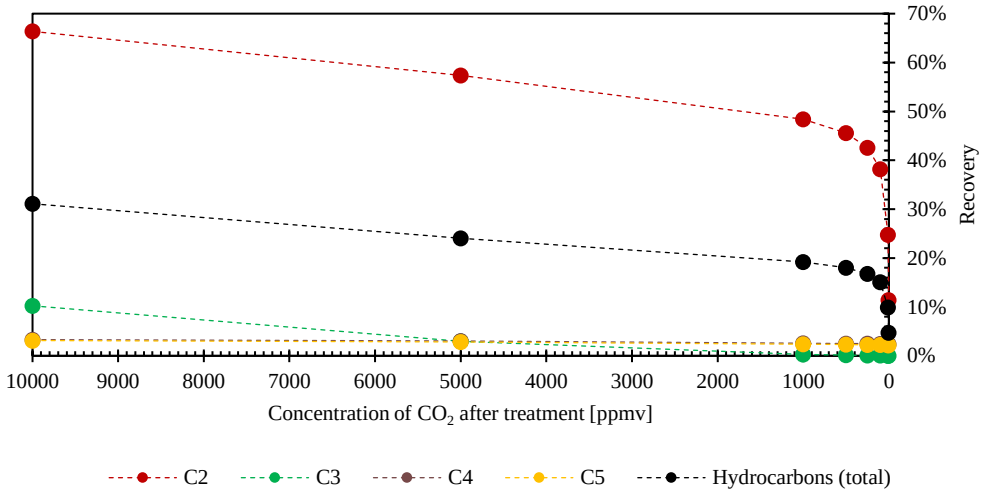

Figure 6.7. Hydrocarbon losses for Rectisol® (sensitivity analysis)

6.2.4 Best alternative

The analysis shows that the energy consumption of Rectisol® is significantly higher than that of amine washes at the working conditions of the process.

Process optimization can decrease the overall energy consumption of Rectisol®, but the sensitivity analysis performed shows that its consumption when aiming low concentrations of CO_2 in the treated gas is excessive. Additionally, the recovery of hydrocarbons is extremely low even when relaxing concentration constraints.

Amine wash is a reliable operation with a relatively low energy consumption and a very high recovery of hydrocarbons. Together with Dow's expertise in its implementation, these factors have contributed to its selection as the best choice.

6.3 Cryogenic distillation

6.3.1 Energy consumption analysis

The results for the energy consumption analysis for the different carbon dioxide recovery technologies assessed are illustrated in Figure 6.8.

Table 6.3 briefly describes each of the alternatives analyzed. Alternatives *X.1* refer to flowsheets purging the distillate of *D-101* and *X.2* to the ones recovering energy from that stream.

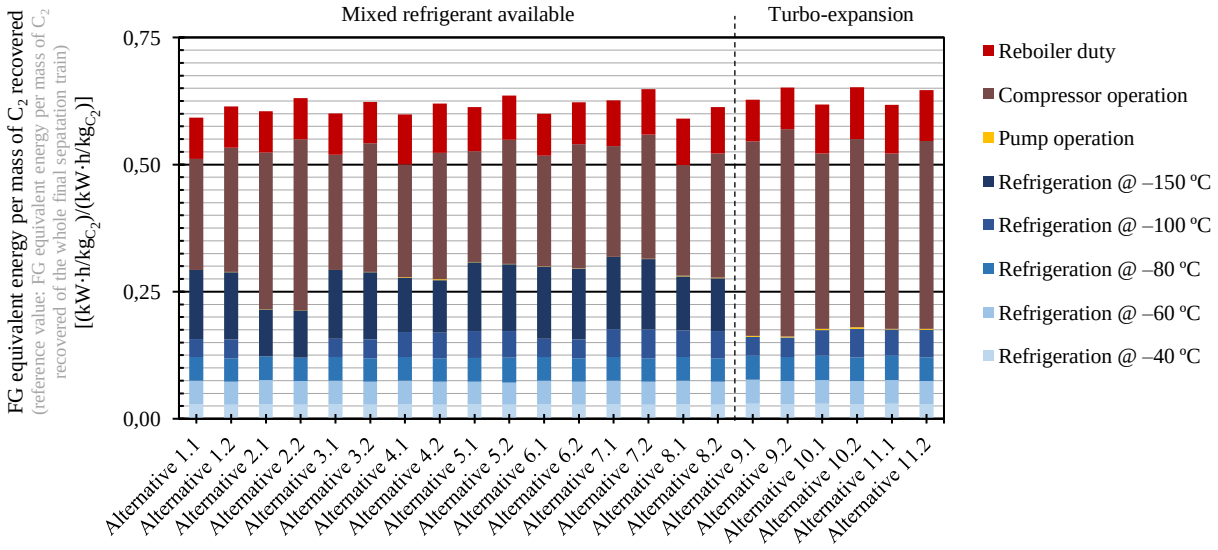

Figure 6.8. Normalized fuel power consumption for the different alternatives for cryogenic distillation. ***Results have been normalized to the energy consumption of the final primary separation unit.***

Table 6.3. Brief description of the alternatives analyzed for cryogenic distillation

Alternative	Description
1	Base case with mixed refrigerant available
2	Modification of alternative 1: turbo-expansion of the syngas recycle stream to provide cooling duty to the condenser of the distillation unit
3	Modification of alternative 1: use of the syngas recycle stream to provide cooling duty to the condenser of the distillation unit
4	Modification of alternative 1: increase of the pressure of the distillation unit to reduce the temperature of the condenser so that an ethylene cycle is used to provide condenser duty
5	Modification of alternative 1: pre-cooling of the feed to decrease condenser duty
6	Modification of alternative 1: feed splitting to decrease the overall energy consumption of the column

Table 6.3. Brief description of the alternatives analyzed for cryogenic distillation (cont.)

Alternative	Description
7	Modification of alternative 1: feed splitting with pre-cooling to decrease the overall energy consumption of the column
8	Modification of alternative 1: feed splitting with increase of the pressure of the distillation unit to reduce the overall energy consumption of the column
9	Base case with turbo-expansion
10	Modification of alternative 9: increase of the pressure of the distillation unit to reduce the temperature of the condenser so that an ethylene cycle is used to provide condenser duty instead of using the syngas recycle stream
11	Modification of alternative 9: increase of the pressure of the distillation unit with feed splitting to reduce the overall energy consumption of the column

The energy consumption analysis shows that the consumption of alternative 8 is the lowest among the scenarios with mixed refrigerant available, and that alternative 11 is the lowest among the scenarios using turbo-expansion.

Some of the main outcomes that can be extracted from the models developed are:

- Reboiler duty is comparable for all the alternatives. As similar compositions and flows are fed to the column and the mass balances aimed are identical, energy consumption is also comparable. Deviations are caused by an increase of pressure in the column or by the pre-cooling of the feed.
- Cooling duty down to -80 °C is comparable for all the alternatives, as the main differences between scenarios are located at the end of the cold box or at the distillation column. Cooling duty at -100 °C is dependent of the energy integration performed with the condenser and differs among alternatives. Cooling duty at -150 °C is only used when the mixed refrigerant is available, and it is also dependent of the energy integration. Alternatives using mixed refrigerant and alternatives using turbo-expansion have different cooling duties. Most scenarios using mixed refrigerant have similar cooling duties and all scenarios using turbo-expansion also do.
- Compression energy differs between alternatives using mixed refrigerant and alternatives using turbo-expansion. Most scenarios using mixed refrigerant have similar compression energy consumption and all scenarios using turbo-expansion also do.
- Compression energy represents between 30 and 60 % of the total energy consumption. This highlights the relevance of working with isobaric processes.
- Pumping energy is negligible compared to the total energy consumption.
- Alternatives using mixed refrigerant have higher cooling duties and lower compression energies, while alternatives using turbo-expansion work the opposite. For scenarios using mixed refrigerant, temperature drop is caused by an external refrigeration cycle,

hence increasing cooling duty and using compressor energy to recover from pressure drops from the process. For scenarios using turbo-expansion, temperature loss is caused by an external refrigeration cycle and by a pressure drop in the process, hence decreasing cooling duty but increasing compressor energy to make-up for the pressure loss.

- Similar energy consumptions are obtained for all the alternatives. This is explained because the energy required to achieve -150 °C in the process is the same regardless of the source of the energy. If the expansion is performed in an external refrigeration cycle, cooling power increases; if the expansion is performed in the process, compression power increases. Small deviations come from the refrigerant (or fluid) being used: CH_4/N_2 for the external refrigeration and H_2/CO for the process expansion.
- All alternatives *X.2* have a slightly lower thermal energy consumption as a result of the thermal integration of the distillate stream in the process. However, the addition of new heat exchangers increases the pressure drop and increases the re-compression energy. As in practice, these heat exchangers would be substituted by a multi-stream plate fin heat exchanger, this pressure drop can be neglected.

Other learnings extracted from the models developed are found in *Appendix 12*, where a more detailed analysis of the results is found. No hydrocarbons are lost during cryogenic distillation.

Figure 6.9 compares the energy consumption of the best alternatives when mixed refrigerant is available and for turbo-expansion.

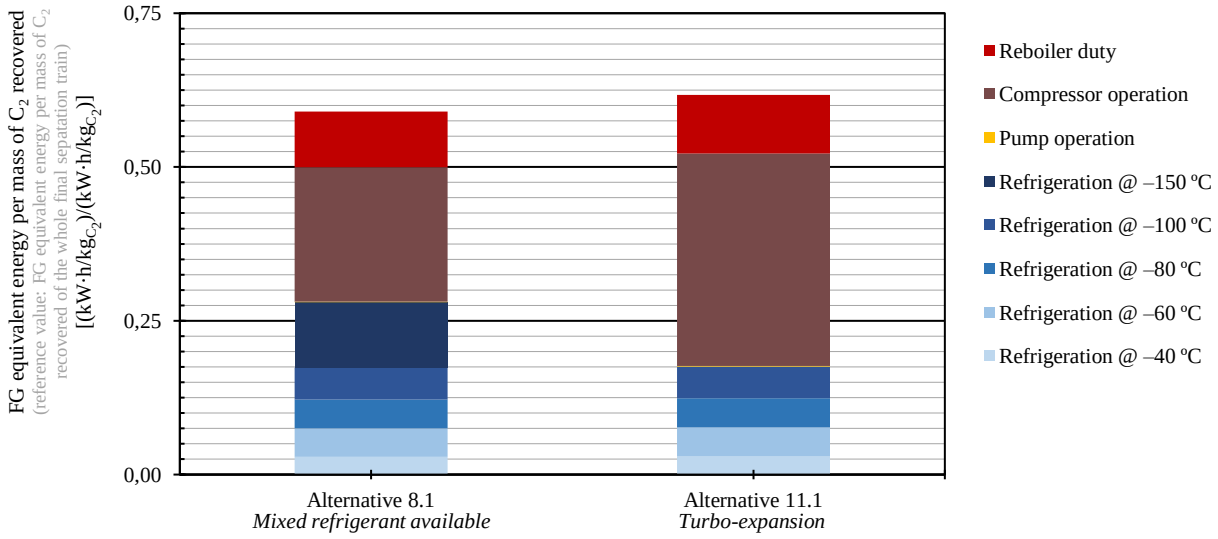

Figure 6.9. Normalized fuel power consumption for the best alternatives for cryogenic distillation. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The analysis shows that the consumption of both alternatives differs by only a 4.5 %. Given the small difference between alternatives, energy consumption cannot be used as the only criterion to select the best configuration.

CAPEX & OPEX analysis are performed to determine the most appropriate technology according to the process needs.

6.3.2 CAPEX and OPEX analysis

The results for the CAPEX analysis for both alternatives compared are illustrated in Figure 6.10. The study has been carried out for a feed basis that results in the same overall C_2&C_3 production and assuming no loss of product or feedstock along the process.

The calculation considers all the units shown in the models and, for the alternative using mixed refrigerant, the compressors from the CH_4-N_2 cycle.

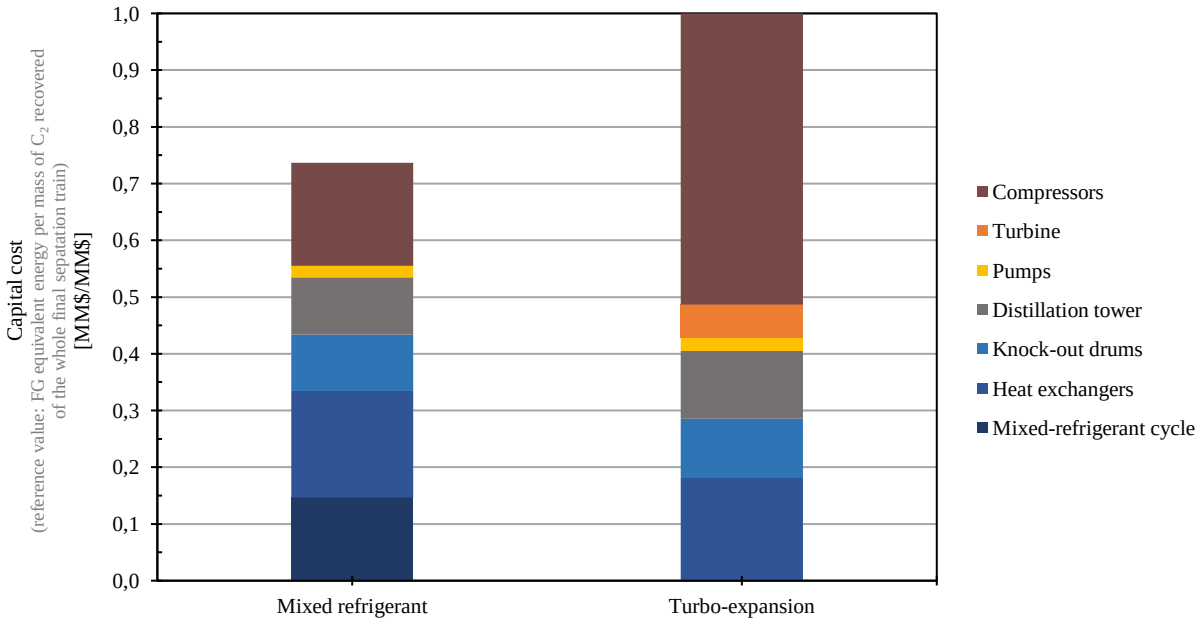

Figure 6.10. CAPEX results for the chosen cryogenic distillation alternatives.
Results have been normalized to the capital cost of the turbo-expansion alternative.

The CAPEX analysis shows that the capital cost of the configuration using mixed refrigerant is lower than the configuration using turbo-expansion.

Some of the main outcomes that can be extracted from the models developed are:

- The installation of the new mixed refrigerant cycle costs around [redacted] MM$.
- Turbo-expansion does not require the installation of a new refrigeration cycle, but the need of an additional compressor and a turbine increase the capital cost of the alternative.

The results for the total annualized cost for both alternatives compared are presented in Table 6.4 (page 69).

Results show that the total annualized cost of the configuration using mixed refrigerant is 6.5% lower than the configuration using turbo-expansion.

Both capital and operational costs are higher for the alternative using turbo-expansion. Hence, the cost of this configuration is always higher than the one using mixed refrigerant regardless of the price of energy.

Table 6.4. Total annualized cost breakdown.

[Table deleted for confidentiality purposes]

6.3.3 Best alternative

Both alternatives have similar energy consumptions and total annualized costs. Although the installation and use of a mixed refrigerant cycle has a cost 6.5 % lower, other criteria must be considered when deciding the best alternative: maintenance, robustness, safety, complexity and controllability, interoperability, experience working with the technology, etc.

In the current process, the use of the alternative using mixed refrigerant requires the installation of the correspondent refrigeration cycle. This adds an increased level of complexity to the operation, as an additional system is operated and additional maintenance expenses appear.

On the other hand, configurations using turbo-expansion are commonly used in the recovery of light olefins generated from steam cracking. This technology is therefore widely used and well understood in the chemical industry, which makes it a favorable option over the installation of a mixed refrigerant cycle if there is no clear benefit in terms of overall energy requirement.

For these reasons, turbo-expansion is chosen as the best alternative to perform the operation in the context of this project.

6.3.4 Comparison of the primary separation unit for light olefins recovery

The performance of cryogenic distillation for the recovery of paraffins from the reactor product (focus of the current project) has been compared to the performance for the recovery of olefins using the same models and updating the necessary parameters.

To compare the process for both chemistries, either the same production of C_2&C_3 or the same feed flowrate can be used. For this study, this last approach has been used. **As a calculation basis, a feed flowrate of 1000 kg/h has been considered. The results obtained are based on this value.**

Results for the energy consumption analysis are illustrated in Figure 6.11.

[Figure deleted for confidentiality purposes]

Figure 6.11. Fuel power consumption comparison between paraffins and olefins recovery main configurations for cryogenic distillation. ***Results have been normalized to the energy consumption of the final primary separation unit.***

**Units of ordinate axis differ from previous figures as the comparison is based on the feed (not on production). Feed flowrate basis of 1000 kg/h.*

The power consumption analysis shows that the consumption of turbo-expansion is similar for both chemistries, and that the consumption of the configuration with mixed refrigerant available is higher for olefins recovery.

Some of the main outcomes that can be extracted from the models developed are described below. Outcomes that can be extracted from the energy consumption mix of only paraffins recovery are already described in *6.3.1. Energy consumption analysis*.

- Refrigeration duty at -150 °C is significantly higher for olefins than for paraffins recovery. Two main reasons justify this behavior:
    - The composition of condensable substances is different for both chemistries. For the paraffins recovery, there are more condensable substances with higher temperature boiling points. This makes that the most part of the refrigeration duty is concentrated at higher temperatures. On the other hand, for olefins recovery there are more condensable substances with lower temperature boiling points. This makes that a significant part of the refrigeration duty is concentrated at -150 °C. This is accentuated by the higher electrical energy consumption of lower temperature refrigeration cycles.
    - The concentration of non-condensable substances is higher for paraffins recovery. This makes the syngas recycle of the process using olefins recovery much smaller than the one used with paraffins recovery. As in the process, the recycle is thermally integrated with the cold box and reduces its energy consumption, less energy is recovered for olefins and, therefore, more energy must be dissipated by the refrigeration cycle.

- Compression energy for paraffins is higher than for olefins recovery in the mixed refrigerant cycle scenarios. Two main reasons justify this behavior:
    - Concentration of incondensable substances. As already explained, the paraffins recovery recycle flowrate is higher due to its higher concentration of incondensable substances. This increases the energy consumption of the compressor, as more flow must be processed.
    - High concentration of hydrogen in paraffins recovery. Given the nature of this molecule, its high concentration increases the consumption of the compressor.
- Compression energy for paraffins and olefins recovery are similar for turbo-expansion. Two different phenomena are acting on opposite directions in this case:
    - High concentration of incondensable substances and of hydrogen in paraffins recovery results on a high consumption of energy in compression.
    - The high concentration of hydrogen in paraffins recovery causes a high temperature drop when is isentropically expanded; so the pressure drop needed to achieve -150 ºC is low. The lower concentration of hydrogen in olefins recovery and the higher concentration of methane causes a lower temperature drop when isentropically expanded; so the pressure drop needed to achieve the same temperature is much higher. This leads to high re-compression energy consumption in olefins recovery to make-up for the pressure drop in the turbine.

Other learnings extracted from the models developed are found in *Appendix 13*, where a more detailed analysis of the results is found.

6.3.5 Comparison with previous work

Results obtained for the olefins recovery in the current project are compared to previous work performed by Soares (2022) to assess the validity of the model developed. The main differences between models are tabulated hereunder.

Table 6.5. Main differences between cryogenic distillation models (current versus previous work)

Current work	Previous work
Refrigerant at 10 °C allocated to water removal	Refrigerant at 10 °C allocated to hydrocarbon recovery
Distillation column design aiming a balance between energy consumption and equipment cost	Distillation column design aiming a minimization of the energy consumption
Energy integration for all the streams	Energy integration for streams lower than -100 °C; for other streams duty is equally distributed.
Pressure loss considered for re-compression	Only re-compression of the expanded syngas is considered

Results for the energy consumption analysis are illustrated in Figure 6.12.

[Figure deleted for confidentiality purposes]

Figure 6.12. Normalized fuel power consumption comparison for olefins recovery between current and previous work for cryogenic distillation. ***Results have been normalized to the energy consumption of the final primary separation unit.***

**Units of ordinate axis differ from previous figures as when considering the olefins recovery both C_2 & C_3 must be considered when normalizing the production.*

Differences between energy consumption are consistent with differences between models:

- Lower reboiler duties and lower refrigeration duty at -150 °C are attributed to the minimization of the energy consumption of the distillation column in previous work.
- Differences in cooling duty above -100 °C are attributed at the energy integration strategy followed. Current work distributes energy from the syngas recycle in the different streams of the cold box according to the needs of the process. Previous work distributes energy from the syngas recycle equally among the different streams of the cold box, increasing the energy consumption.
- Compression energy is relatively small for the configuration using mixed refrigerant in the current work because the compressor only has to make-up for pressure drop along the process; this is not considered in previous work. In a similar way, compression energy for the case with turbo-expansion is higher for current work because the pressure drop is considered.

6.4 Extractive distillation

6.4.1 Energy consumption analysis

The results for the energy consumption analysis for the different carbon dioxide recovery technologies assessed are illustrated in Figure 6.13 (page 73).

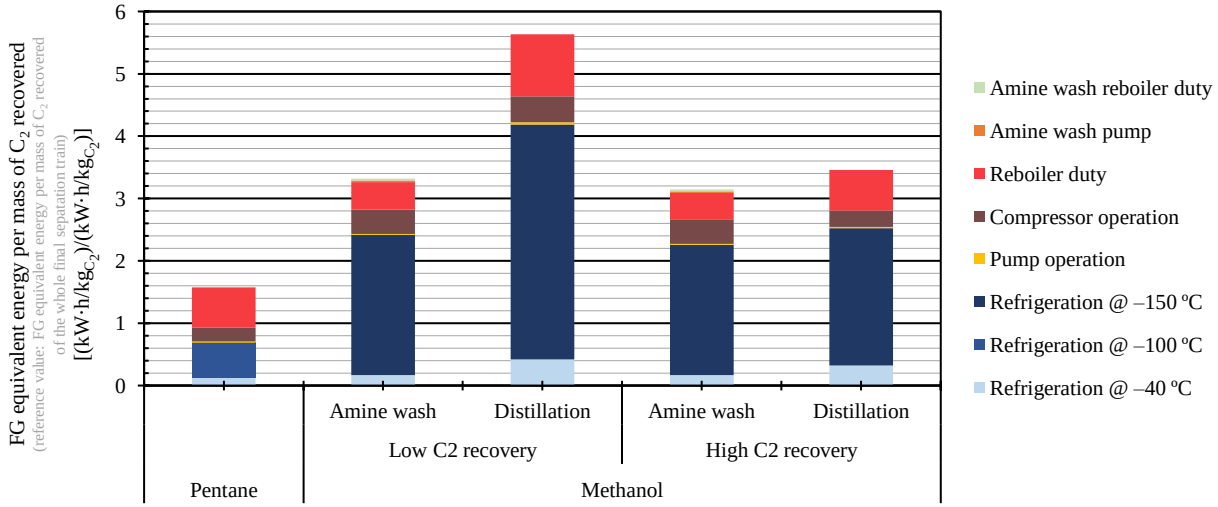

Figure 6.13. Normalized fuel power consumption for the alternatives of extractive distillation. ***Results have been normalized to the energy consumption of the final primary separation unit.***

**Temperature of the gaseous feed of the extractive distillation column: -40 °C*
Solvent to C_2 feed ratio of 5 (pentane) and 13 (methanol)

The energy consumption analysis shows that extractive distillation using pentane is the configuration with the lowest energy among the scenarios studied.

Some of the main outcomes that can be extracted from the models developed are:

- Reboiler duties of all the configurations are of the same order of magnitude. To better explain this occurrence, Figure 6.14 represents the distribution of reboiler duties among the different columns. Outcomes from this figure are found in the next page.

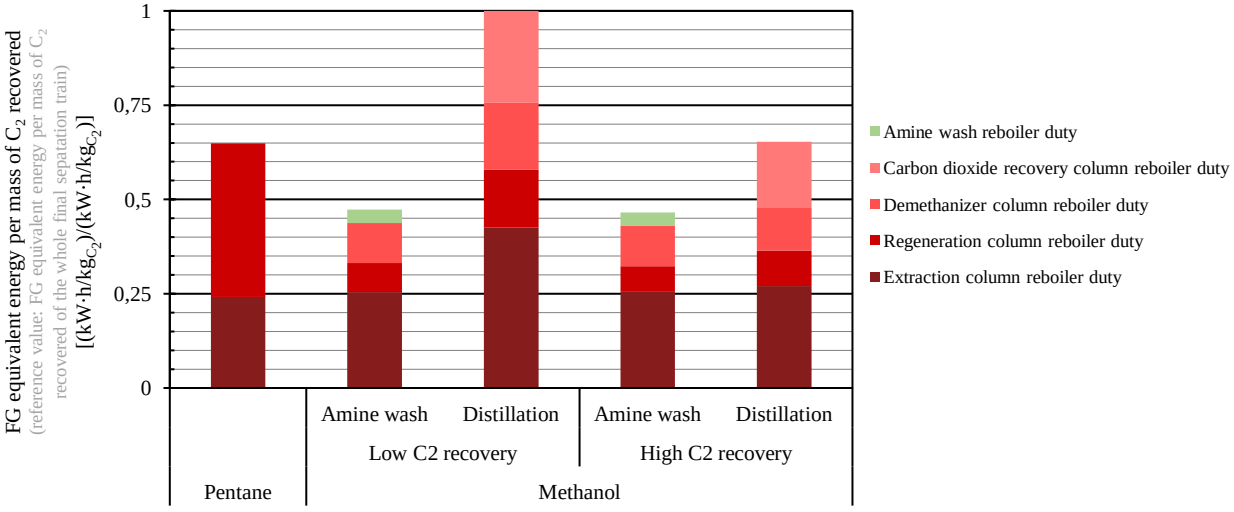

Figure 6.14. Normalized fuel power consumption for the alternatives of extractive distillation (only reboiler duties). ***Results have been normalized to the energy consumption of the final primary separation unit.***

Outcomes extracted from the reboiler duty analysis are listed hereunder. Figure 6.14 represents the consumption normalized per product. This means that, even for the same energy consumption per feed basis, the normalized value can be higher if the recovery of product is low (as it is the case of the configuration using methanol, with a low C_2 recovery in the extractive distillation column and a recovery of CO_2 using distillation).

- Reboiler duties of extraction columns are of the same order of magnitude. Although methanol columns operate with a higher flowrate of solvent than pentane columns, temperature differentials between condensers and reboilers are significantly lower.

- Reboiler duty of the pentane regeneration column is significantly higher than that of methanol regeneration columns. This is caused by the simple regeneration of methanol when compared to pentane: only a small reflux and boiling rate is needed to achieve the specifications of the regenerated solvent.

- Reboiler duties of the demethanizer columns and the carbon dioxide recovery column are similar for all the alternatives that use them, as similar compositions and flowrates are fed to the column in all the configurations.

- Reboiler duties of the amine washes are negligible when compared to the total heating energy consumption.

- There is a balance of the energy consumption of all the configurations because of: 1) the high energy consumption of the pentane extractive distillation column, 2) the low energy consumption of the same column for methanol and 3) the increase of total reboiler duty for methanol cases caused by the presence of additional columns. This balance and the relativization of reboiler duty when compared to the total energy consumption make that the use of heating energy is comparable for all the configurations.

- Cooling duties for pentane and for methanol are different. To better explain this occurrence, Figure 6.15 (page 75) represents the distribution of cooling duties among the different processes.

  Note that Figure 6.15 represents the consumption normalized per product, so even for the same energy consumption per feed basis, the normalized value can be higher if the recovery of product is low.

  - Cooling duties of *HE-102* and *HE-104* (feed cooling) are of the same order of magnitude for all the configurations. Cooling energy is slightly higher for alternatives using methanol, as there is more solvent to refrigerate. As the solvent flowrate is higher, more energy from the syngas recycle is used to decrease the temperature of the solvent and there is less available to decrease the temperature of the feed.

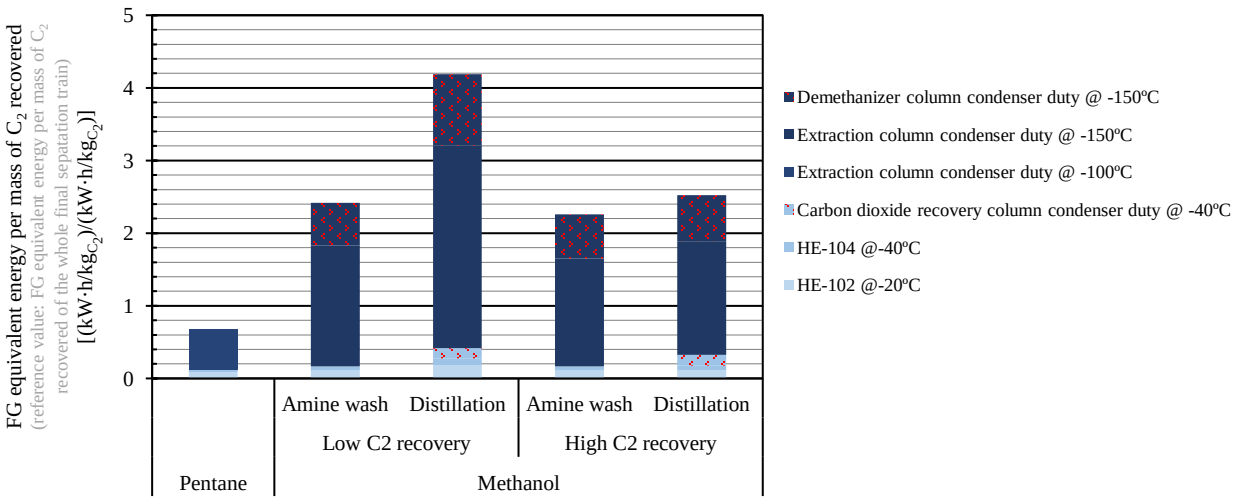

Figure 6.15. Normalized fuel power consumption for the alternatives of extractive distillation (only cooling duties). ***Results have been normalized to the energy consumption of the final primary separation unit.***

- Condenser duties of methanol extraction columns (at -150 °C) are higher than that of pentane (at -100 °C). Three reasons explain this behavior: 1) methanol solvent flowrate is significantly higher than pentane solvent flowrate, 2) temperature differential of methanol in the condenser is higher than that of pentane and 3) electric energy to refrigeration energy conversion factors for cooling duty at -150 °C are lower than those at -100 °C.

- Demethanizer condenser duties are of the same order of magnitude, as similar compositions and flowrates are fed to the column in all the configurations.

- Compressor energy consumption is of the same order of magnitude, but slightly higher for methanol configurations. A most CO_2 is recovered at low pressure in these alternatives, there is the need to use additional energy to re-compress CO_2.

Therefore, pentane is the chosen solvent to assess extractive distillation as a hydrocarbon recovery technology. Other learnings extracted from the models developed are found in *Appendix 15*, where a more detailed analysis of the results is found.

Different sensitivity analysis are performed for the configuration using pentane as entrainer to determine the variables that minimize the overall energy consumption of the process.

6.4.2 Analysis of the influence of flowrate of solvent

The results for solvent flowrate sensitivity analysis are illustrated in Figure 6.16 (page 76).

To perform the analysis, the solvent flowrate has been modified while maintaining process specifications (mass balance) and other variables constant. The base model is the one used for pentane in *6.4.1. Energy consumption analysis* (initial solvent to C_2 feed ratio of 5).

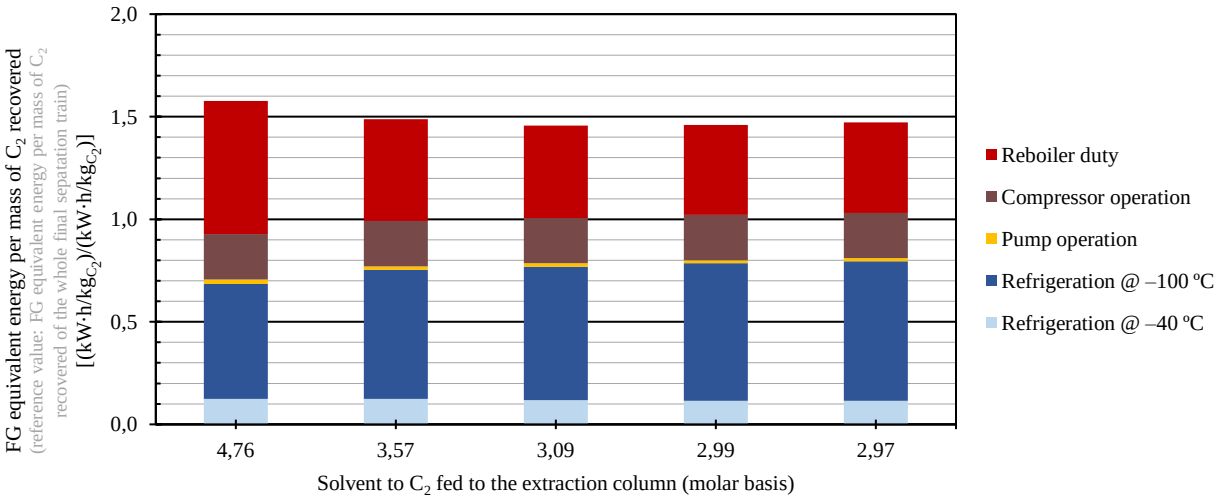

Figure 6.16. Normalized fuel power consumption for different solvent to C_2 ratios for extractive distillation with pentane. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The energy consumption sensitivity analysis shows that solvent to C_2 feed ratio of 3.1 is the configuration with the lowest energy among the scenarios studied.

Some of the main outcomes that can be extracted from the sensitivity analysis are:

- Reboiler duty has a minimum at a solvent to C_2 feed ratio of 3.1. To better explain this occurrence, Figure 6.17 represents the distribution of reboiler duties among the different columns. Outcomes from this figure are found in the next page.

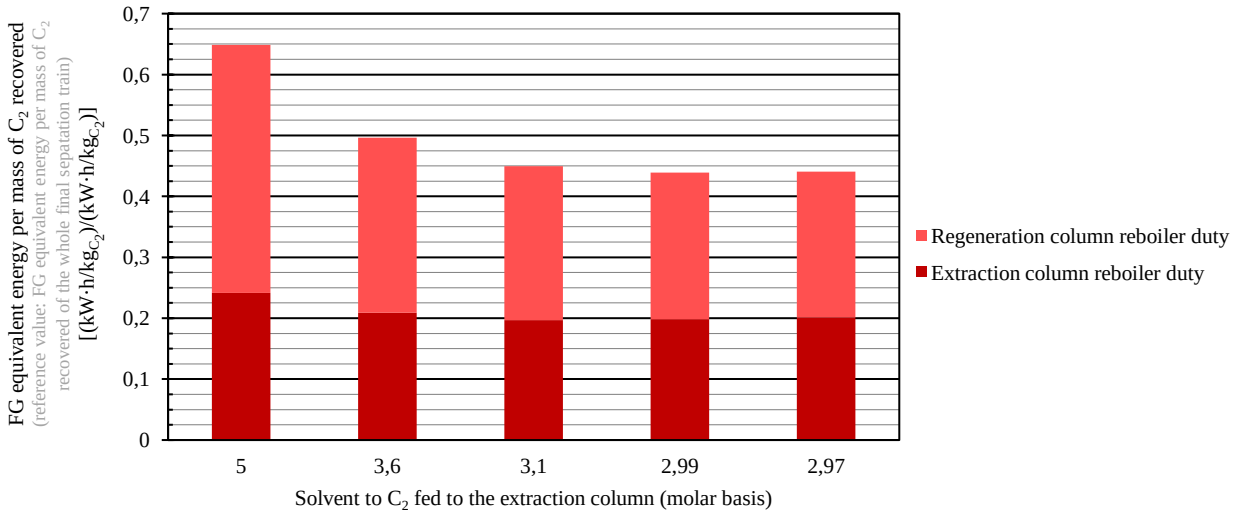

Figure 6.17. Normalized fuel power consumption for different solvent to C_2 ratios for extractive distillation with pentane (only reboiler duties). ***Results have been normalized to the energy consumption of the final primary separation unit.***

  - Extraction column reboiler duty has a minimum at 3.1. The lower the solvent flowrate, the lower the flowrate of solvent that must be heated to the temperature of the reboiler and, therefore, the lower the energy consumption of the reboiler. However, as the solvent acts as an entrainer, a reduction of the solvent to C_2 ratio increases the energy required to perform the separation (constant mass balance). Both phenomena combine to create a minimum.
  - Regeneration column reboiler duty decreases when the solvent to C_2 ratio does. As there is less solvent to regenerate, the consumption of energy is also reduced.

- Cooling duty increases when solvent to C_2 feed ratio decreases. This variation is caused mainly by the extractive distillation column condenser (refrigeration at -100 °C). Solvent in the column is acting as external condenser. When the solvent flowrate is reduced, condenser duty must increase to provide the cooling energy that the solvent was previously providing and maintain constant the mass balance of the column.
- Compressor energy is not affected by the solvent to C_2 feed ratio.
- Pumping energy decreases as solvent ratio does, as there is less solvent to be re-compressed. Given that the source of most part of the energy consumption is heating and cooling duties and compression energy, this effect is practically negligible.
- When all the trends mentioned are combined, energy consumption has a minimum at the solvent to C_2 feed ratio of 3.1.

Other learnings extracted from the sensitivity analysis are found in *Appendix 16*, where a more detailed analysis of the results is found.

Based on the results obtained, the best solvent to C_2 feed ratio among the values studied in the conditions of the analysis is 3.1. Following sensitivity analysis are carried out using this value.

6.4.3 Analysis of the influence of the temperature of the feed

The results for the feed temperature sensitivity analysis are illustrated in Figure 6.18 (page 78).

To perform the analysis, the temperature of the feed has been modified while maintaining process specifications (mass balance) and other variables constant. The base model is the one used for pentane in *6.4.1. Energy consumption analysis* (initial feed temperature of -40 °C), modifying the solvent to C_2 feed ratio to 3.1.

The energy consumption sensitivity analysis shows that feed temperature of -60 °C is the configuration with the lowest energy among the scenarios studied.

Some of the main outcomes that can be extracted from the sensitivity analysis are:

- Cooling duty has a minimum at -60 °C. Feed refrigeration (i.e., refrigeration duties at -40, -60 and -80 °C) increases when the temperature of the feed decreases. When the temperature of the feed is reduced, the energy that the condenser must dissipate from the gas is lower, reducing its energy consumption.

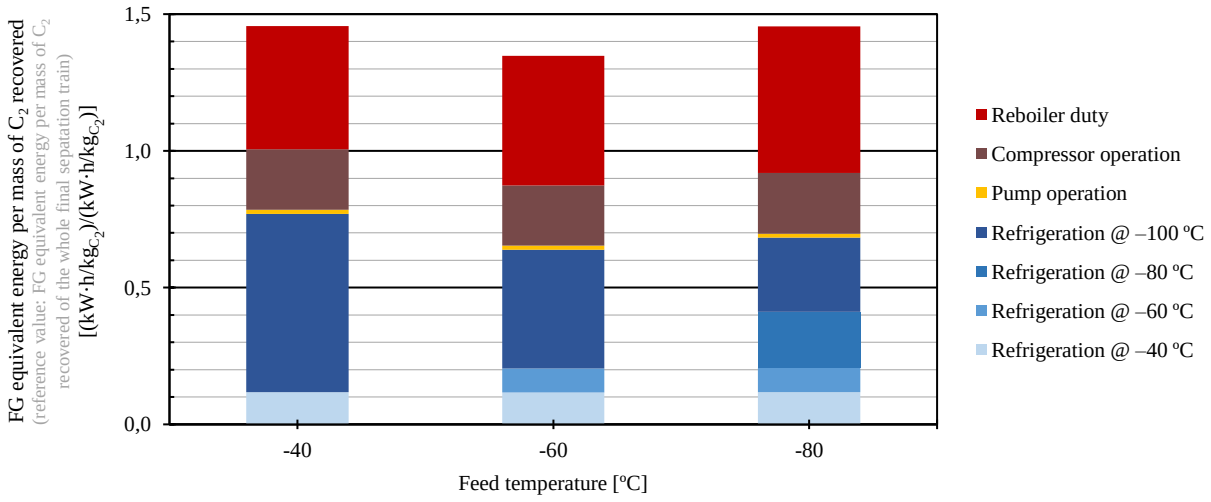

Figure 6.18. Normalized fuel power consumption for different feed temperatures for extractive distillation with pentane. ***Results have been normalized to the energy consumption of the final primary separation unit.***

- Reboiler duties increase when the temperature of the feed decreases. As the temperature of the feed is reduced, the consumption of the reboiler from the extractive distillation column increases to make up for the reduction of temperature. The reboiler duty of the regeneration column is maintained constant.
- Pump and compression energy are not affected by the feed temperature.
- When all the trends mentioned are combined, energy consumption has a minimum at the feed temperature of -60 °C.

Other learnings extracted from the sensitivity analysis are found in *Appendix 17*, where a more detailed analysis of the results is found.

Based on the results obtained, the best feed temperature among the values studied in the conditions of the analysis is -60 °C. Following sensitivity analysis are carried out using this value.

6.4.4 Analysis of the influence of the purity of the regenerated solvent

The results for the regenerated solvent purity sensitivity analysis are illustrated in Figure 6.19 (page 79).

To perform the analysis, the purity of the regenerated solvent has been modified while maintaining process specifications (mass balance) and other variables constant. The base model is the one used for pentane in *6.4.1. Energy consumption analysis* (initial purity of the regenerated solvent of [redacted] %), modifying the solvent to C_2 feed ratio to 3.1 and the feed temperature to -60 °C.

The energy consumption sensitivity analysis shows that a purity of the solvent of 95 % is the configuration with the lowest energy among the scenarios studied with acceptable recovery of propane in the regeneration column.

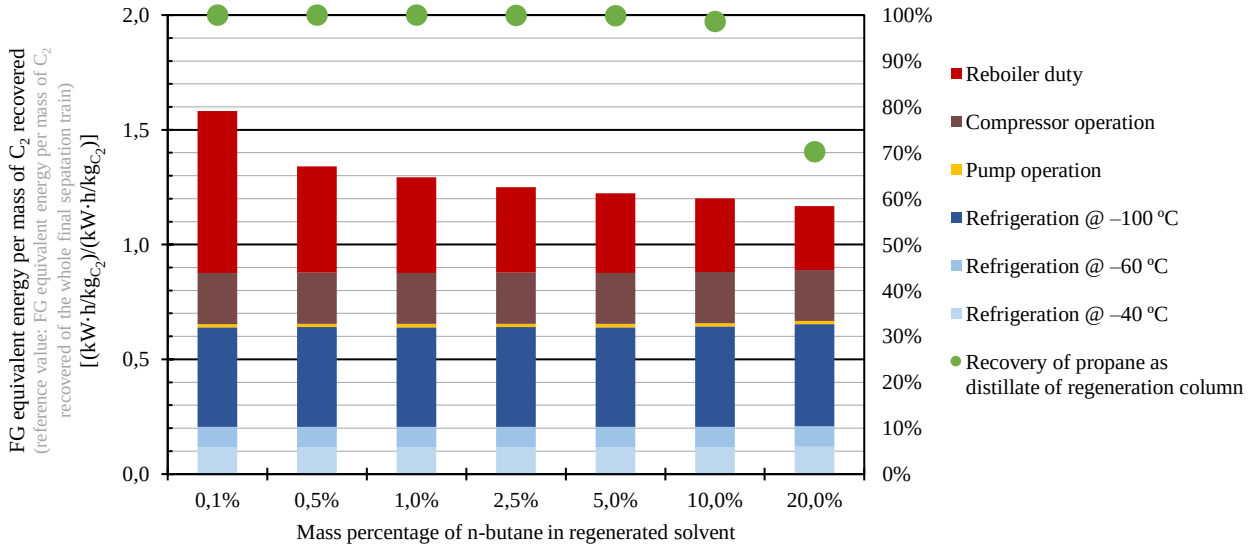

Figure 6.19. Normalized fuel power consumption for different feed solvent purities for extractive distillation with pentane. ***Results have been normalized to the energy consumption of the final primary separation unit.***

Some of the main outcomes that can be extracted from the sensitivity analysis are:

- Cooling duty is not affected by the purity of the solvent. As cooling energy using refrigeration cycles is only used in the feed and in the extractive distillation column, the effect of the purity of the solvent is marginal.
- Reboiler duty is reduced when the purity of the solvent decreases. As the constraints of purity of the regenerated solvent are relaxed, the energy required by the reboiler duty of the regeneration column to achieve the specifications is lower. Reboiler duty of the extractive distillation column is not affected by the purity of the solvent.
- Pump and compression energy are not affected by the feed temperature.
- The recovery of propane as distillate in the regeneration column decreases as the purity of the solvent decreases. As the constraints of purity of the regenerated solvent are relaxed, more species other than the solvent are obtained by bottoms of the regeneration column. This increases the loss of product or other process hydrocarbons.

Other learnings extracted from the sensitivity analysis are found in *Appendix 18*, where a more detailed analysis of the results is found.

Based on the results obtained and stablishing an additional constrain of propane recovery at the top of the regeneration column of 99 % to avoid loss of product, the best solvent purity among the values studied in the conditions of the analysis is 95 %. Following sensitivity analysis are carried out using this value.

6.4.5 Analysis of the influence of the recovery of solvent by bottoms in the regeneration column

The results for the solvent recovery sensitivity analysis are illustrated in Figure 6.20.

To perform the analysis, the recovery of solvent by bottoms of the regeneration column has been modified while maintaining process specifications (mass balance) and other variables constant. The base model is the one used for pentane in *6.4.1. Energy consumption analysis* (initial recovery of solvent by bottoms of [redacted] %), modifying the solvent to C_2 feed ratio to 3.1, the feed temperature to -60 °C and the purity of the regenerated solvent to 95 %.

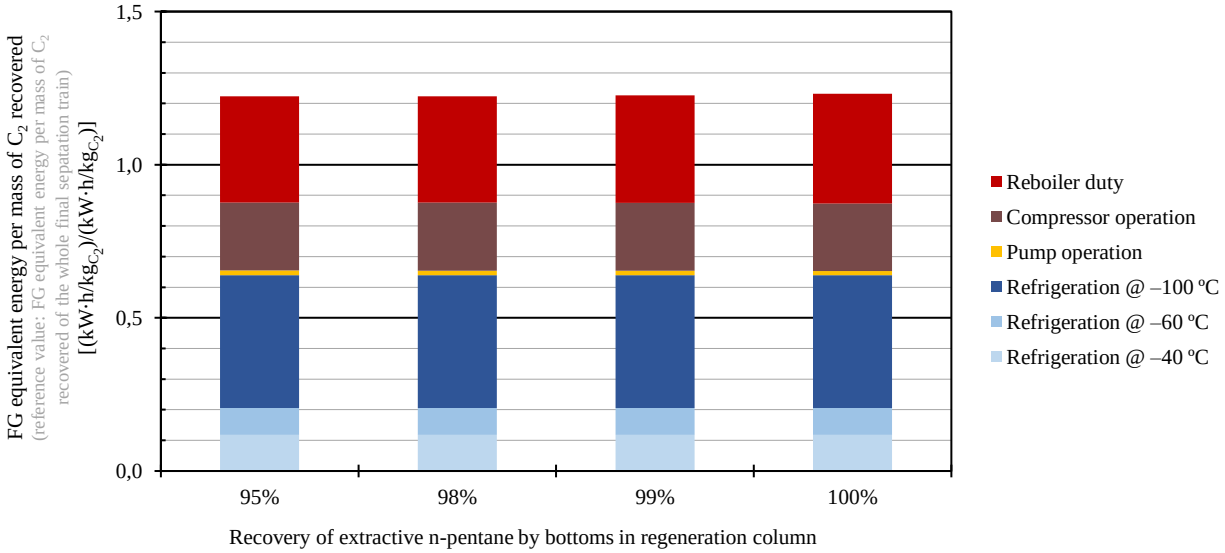

Figure 6.20. Normalized fuel power consumption for different solvent recoveries for extractive distillation with pentane. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The energy consumption sensitivity analysis shows that the influence of the recovery of solvent by bottoms of the regeneration column in the energy consumption is marginal. When establishing the purity of the solvent using the key light component (n-butane), the system already works recovering a high percentage of solvent. When pushing the system to recover more solvent, the energy required to achieve the new specification is minimal.

Other learnings extracted from the sensitivity analysis are found in *Appendix 19*, where a more detailed analysis of the results is found.

Based on the results obtained, a recovery of 100 % is aimed in the process. Given that there is no energy penalty at targeting a full recovery, this simplifies the process as a make-up system is not required. In practice, the installation of this system is needed, as small leaks may exist in the equipment.

6.4.6 Analysis of the influence of the extraction column CO_2 removal capacity

The results for the extraction column CO_2 removal capacity sensitivity analysis are illustrated in Figure 6.21.

To perform the analysis, the reboiler duty of the extractive distillation column has been modified to vary the concentration of CO_2 at the inlet of the amine wash, while maintaining process specifications (mass balance) and other variables constant. The base model is the one used for pentane in *6.4.1. Energy consumption analysis* (initial concentration of CO_2 at the inlet of the amine wash of [redacted] ppmv), modifying the solvent to C_2 feed ratio to 3.1, the feed temperature to -60 °C, the purity of the regenerated solvent to 95 % and the recovery of solvent to 100 %.

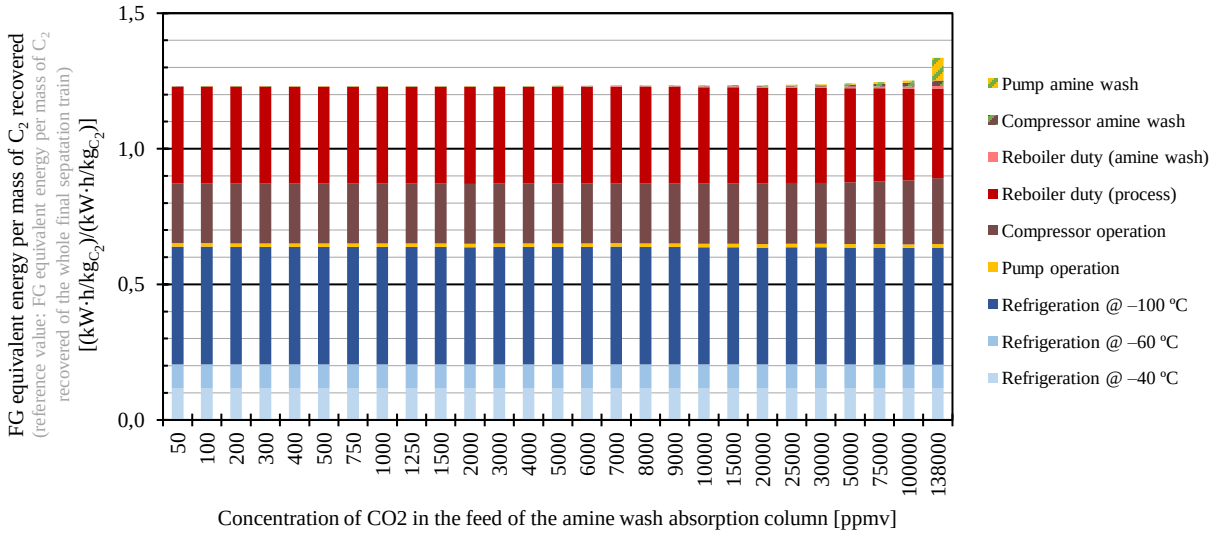

Figure 6.21. Normalized fuel power consumption for different CO_2 concentrations in the feed of the amine wash for extractive distillation with pentane. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The energy consumption sensitivity analysis shows that the concentration of CO_2 at the inlet of the amine wash with the lowest energy among the scenarios studied is 400 ppmv.

Some of the main outcomes that can be extracted from the sensitivity analysis are:

- Cooling, pumping and compression energy are barely affected by the concentration of CO_2 at the inlet of the amine wash.
- Reboiler duty decreases when the concentration of CO_2 at the inlet of the amine wash system increases. When relaxing the concentration of light key (carbon dioxide) at the bottom, the energy required to perform the separation decreases and the reboiler duty of the extractive distillation column decreases too.
- Amine wash related energy increases when the concentration of CO_2 at the inlet of this system increases, as the amine process has to use more energy to completely remove the carbon dioxide from the stream.

Other learnings extracted from the sensitivity analysis are found in *Appendix 20*, where a more detailed analysis of the results is found.

Although the minimal energy consumption of the system is found when the concentration of CO_2 at the inlet of the amine wash is 400 ppmv, the difference of consumption with respect a concentration of 50 ppmv is minimal. As this last concentration avoids the installation of an amine wash process and the energy penalty by doing so in minimal, 50 ppmv of CO_2 are aimed in the product stream.

6.5 Comparison of hydrocarbon recovery alternatives: cryogenic and extractive distillations

The results for the energy consumption analysis for the final alternatives of the hydrocarbon recovery technologies assessed are illustrated in Figure 6.22.

The energy consumption associated with amine washing is included for cryogenic distillation, whereas the energy consumption related to TSA for water removal is not considered. Its omission in the figure is due to its requirement in both configurations. However, extractive distillation does not require amine washes to achieve the CO_2 specifications in the product, so it must be included in cryogenic distillation for the purpose of a comprehensive comparison.

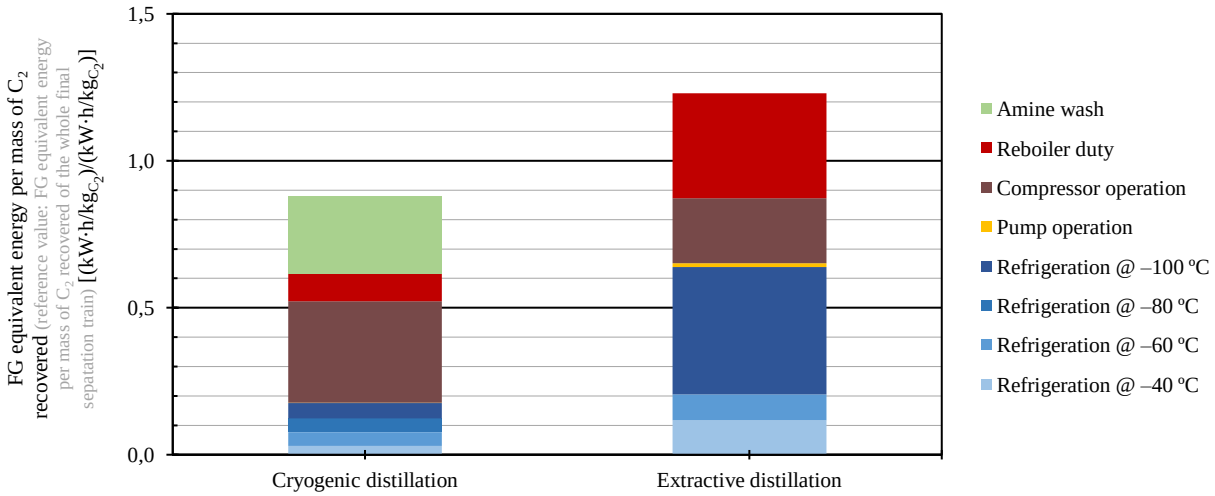

Figure 6.22. Normalized fuel power consumption for the options for hydrocarbon recovery. ***Results have been normalized to the energy consumption of the final primary separation unit.***

The energy consumption analysis shows that cryogenic distillation is the configuration with the lowest energy consumption.

Some of the main outcomes that can be extracted from the sensitivity analysis are:

- Cooling duty is significantly higher for extractive distillation because of the operation with solvent. When operating cryogenic distillation, all the thermal energy extracted from the system is dedicated to the condensation of hydrocarbons from the feed gas. When operating extractive distillation, in addition to the energy required to condense hydrocarbons, there is the need to cool down the solvent.

- Pumping energy is higher for extractive distillation, as the process must re-pressurize the solvent after the regeneration column.
- Reboiler duty is significantly higher for extractive distillation. The main reasons of this behavior are: 1) cryogenic distillation needs to operate only a demethanizer column, while extractive distillation needs to operate an extraction column and a regeneration column and 2) the presence of solvent in extractive distillation increases the energy consumption, as part of the energy supplied to the system is dedicated to heat the solvent.
- Compression energy is higher for cryogenic distillation. As this configuration uses turbo-expansion to operate at temperatures of -150 °C, there is an additional pressure drop that is not present in extractive distillation, increasing the compression energy.
- Amine wash is present only for cryogenic distillation.

As cryogenic distillation has the lowest energy consumption among the alternatives assessed, it is the alternative chosen to perform the recovery of hydrocarbons in the process.

6.6 Energy consumption analysis and flowsheet of the final process

The results for the energy consumption analysis for the final process is illustrated in Figure 6.23. Some of the main outcomes that can be extracted from the sensitivity analysis are found in the next page. The flowsheet of the final process is illustrated in Figure 6.24.

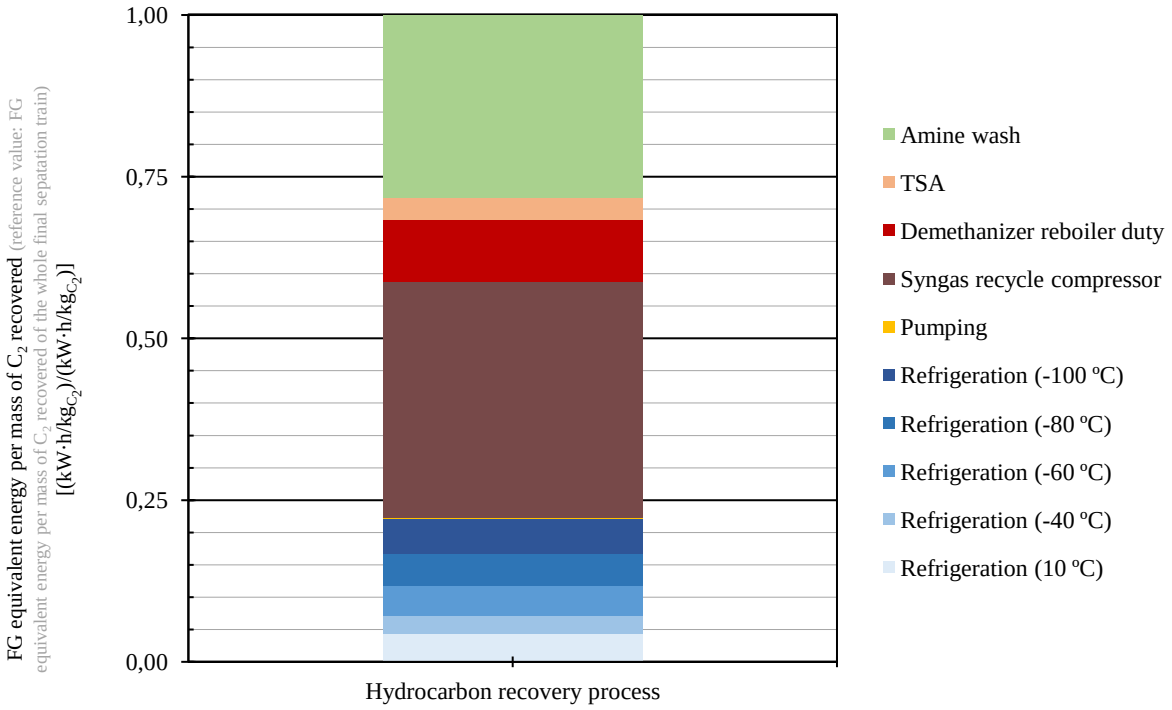

Figure 6.23. Normalized fuel power consumption for the paraffins recovery process.
Results have been normalized to the energy consumption of the final primary separation unit.

Some of the main outcomes that can be extracted from the analysis are:

- When comparing TSA, amine wash and cryogenic distillation (composed of refrigeration, pumping, syngas recycle compressor and demethanizer reboiler duty), cryogenic distillation is the section with the highest energy demand of the process. Its consumption is, approximately, 2/3 of the total energy consumption of the process. This is coherent, as cryogenic distillation operates at very low temperatures and re-pressurization expenses of the process are assigned to this operation.

- Amine wash constitutes, approximately, 25% of the total energy consumption of the process. This is coherent, as re-compression expenses of recovered CO_2 are assigned to this operation and represents, approximately, 1/3 of the amine wash total energy consumption. Additionally, the low partial pressure of carbon dioxide in the gas increases the overall power consumption of this operation, as already described in *6.2.2. Energy consumption analysis*. The breakdown of the energy consumption of amine washes is found in Appendix 10.

- Reboiler duty of the demethanizer represents barely a 10 % of the total energy consumption of the system. Although its consumption can be reduced to increase the energy efficiency of the process, improvement of other unit operations can result in larger impacts on energy consumption.

- Compression of the syngas recycle is the most energy consuming operation of all the process and represents more than 1/3 of the total energy consumption of the process. The re-compressed stream is mainly composed of hydrogen. As already explained in *4.5. Hydrogen recovery*, hydrogen compression is energy-intensive given its low molecular weight and its high compressibility factor. This fact, together with the high flowrate of syngas recycle and the need of turbo-expanding the stream to achieve low temperatures, makes compression the unit operation with the highest energy consumption.

- Refrigeration duty represents almost 25 % of the total energy consumption of the process. Despite representing a significant fraction of the total energy consumption, it is still relatively low considering the low temperatures achieved and the large flowrate of gas to be cooled. As already described in *6.3.4. Comparison of the primary separation unit for light olefins recovery*, the large flowrate of the syngas recycle helps reducing the cooling duty of the cold box. As the recycle must exit the process at around 35 °C, the stream is used to dissipate heat from the streams of the cold box, significantly reducing the cooling duty provided by refrigeration cycles.

- Both last points highlight the relevance of the syngas recycle in the hydrocarbon recovery process. On the one hand, its recompression substantially increases the energy consumption of the system; on the other hand, it significantly reduces the cooling duty provided by external refrigeration cycles.

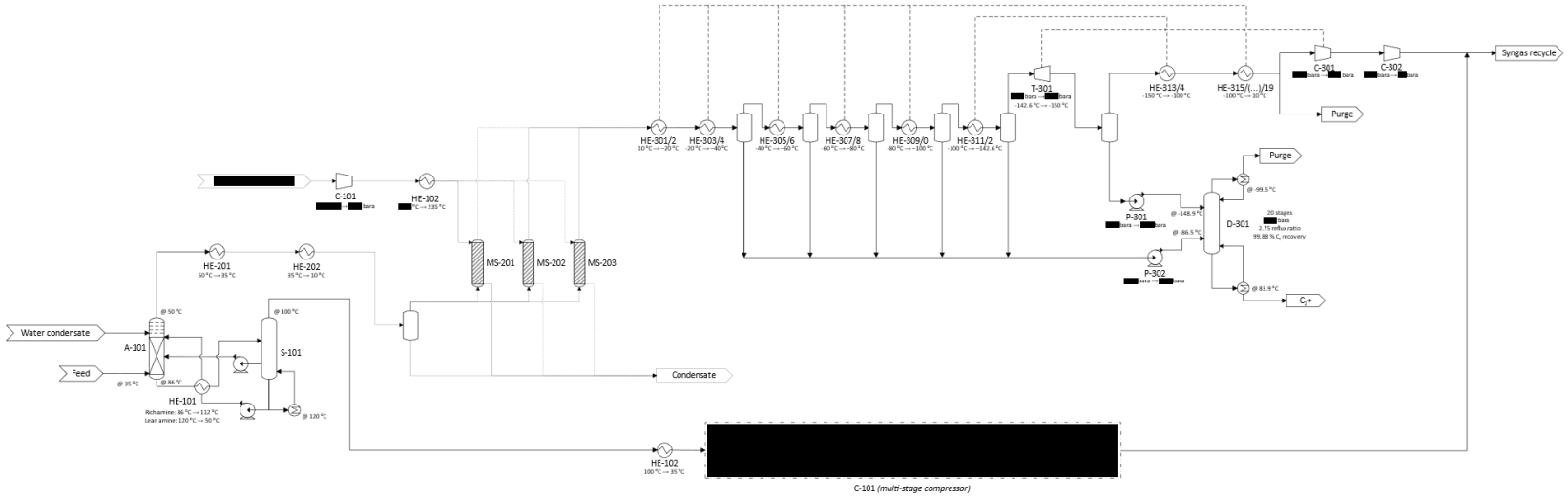

Figure 6.24. Flowsheet of the paraffins recovery process.

[This page intentionally left blank]

7 CONCLUSIONS

The proposed separation train for the recovery of hydrocarbons from the outlet mixture of the syngas conversion reactor comprises three distinct steps: amine washing for carbon dioxide recovery, molecular sieving for water removal, and cryogenic distillation with turbo-expansion for hydrocarbon recovery.

Regarding carbon dioxide recovery, amine washing demonstrated an energy consumption of [redacted] $kW \cdot h/kg_{C_2}$. This consumption is 10 times lower than that of Rectisol® under the specified process conditions and aiming at the desired carbon dioxide concentration in the treated gas.

The higher energy consumption observed in Rectisol® can be attributed to three factors. (i) Sensitivity analyses indicate that methanol exhibits a strong affinity for hydrocarbons. This leads to a reduced recovery of hydrocarbons that results in increased energy requirements for the same production basis. (ii) Aiming for low concentration of carbon dioxide in the treated gas results in higher energy consumption due to the low partial pressure of carbon dioxide in the feed. (iii) Partial solvent regeneration in amine washing further reduces energy consumption.

For water removal, TSA was the chosen method, as it was found to be the most suitable alternative. Molecular sieving exhibited an energy consumption of [redacted] $kW \cdot h/kg_{C_2}$, which is 13 times lower than that of glycol absorption under the specified process conditions and aiming at the desired water concentration in the treated gas.

The higher energy consumption observed in glycol absorption can be attributed to the low concentration of water aimed in the treated gas. This results in increased energy requirements due to the low partial pressure of water in the feed. However, the sensitivity analyses conducted reveal that when targeting a higher concentration of water in the treated gas, glycol absorption exhibits a lower energy consumption compared to TSA under the revised conditions. As a result, combining glycol absorption with molecular sieving becomes a viable option. In this approach, glycol absorption is used for bulk removal of water, while TSA is employed for polishing purposes. An economic assessment should be conducted to determine the feasibility of this alternative.

Cryogenic distillation was selected as the preferred technology for hydrocarbon recovery. It demonstrated an energy consumption of [redacted] $kW \cdot h/kg_{C_2}$, considering the previous amine wash step required. In contrast, extractive distillation exhibited an energy consumption of [redacted] $kW \cdot h/kg_{C_2}$, making it 1.5 times higher than cryogenic distillation.

The higher energy consumption in extractive distillation is attributed to the presence of solvent. In general, solvent increases energy requirements, as it involves processing not only the gas and the hydrocarbons, but also a substantial amount of solvent. The increment of relative volatility between C_2 and carbon dioxide, which simplifies the separation, did not justify the use of solvent or the installation of an additional column (regeneration column) to accommodate it.

To achieve process temperatures of -150 °C for cryogenic distillation, the feasibility of using a mixed refrigerant cycle and a turbo-expander was assessed as a means of complementing the existing refrigeration cycles. Both alternatives exhibited similar energy requirements. This is attributed to the fact that the energy needed to attain -150 °C in the process remains constant regardless of the energy source utilized. If the expansion is performed within an external

refrigeration cycle, cooling power increases; conversely, if the expansion occurs within the process, re-compression power increases. Slight deviations arise from the refrigerant or fluid expanded, with CH_4/N_2 selected for external refrigeration and H_2/CO used in process expansion.

Given the comparable energy consumption, CAPEX and OPEX analysis were conducted to determine the most suitable strategy. However, both options yielded comparable total annualized costs. Therefore, additional criteria were taken into account, such as avoiding the installation of supplementary facilities within the plant. Based on these considerations, turbo-expansion emerged as the most feasible strategy.

The cryogenic distillation model was modified to accommodate the olefins recovery and was subsequently used to compare the models developed within this project with those previously designed by Soares (2022). The outcomes derived from the model developed within this project align closely with those obtained in the earlier work, thus confirming the validity and reliability of the models developed within the scope of this project.

Remaining non-condensable gases (mainly syngas) are re-pressurized and directed back to the syngas conversion reactor, with the re-compression accounting for approximately 35 % of the overall energy consumption in the process. This significant energy consumption can be attributed to the compression of hydrogen, which is known to be energy intensive. Additionally, the recycle stream itself is of considerable magnitude, further contributing to the overall energy requirements. However, this stream also serves a crucial role in the energy integration of the process.

As the recycle stream undergoes cooling to -150 °C within the process and needs to exit at around 35 °C, it is utilized to dissipate energy in the cold box through heat integration with a multi-stream plate fin heat exchanger. This integration substantially reduces the overall energy consumption of the system. Therefore, the flowrate of the recycle stream plays a pivotal role in determining the energy consumption. On one hand, an increase in flowrate leads to higher compression power, while on the other hand, it reduces the energy consumption of the cold box. This relationship is evident in the comparison between the models developed for olefins recovery and paraffins recovery. Effective coordination between the teams working on process development and chemistry is vital to minimize the total energy consumption by modifying the product/syngas ratio and, consequently, adjusting the recycle flowrate.

Similarly, the composition of this stream significantly impacts the process expenses. In addition to the concentration of all non-condensable species, which is directly associated with the recycle flowrate, the concertation of hydrogen plays a crucial role in turbo-expansion. Since the pressure drop required to reach -150 °C is primarily dependent on the hydrogen fraction present in the gas, it directly impacts the re-compression energy required.

In conclusion, the proposed separation train for hydrocarbon recovery comprising amine washing, molecular sieving and cryogenic distillation with turbo-expansion has been successfully evaluated in this project. The chosen strategies demonstrated lower energy consumption to alternative options. It has also been demonstrated that the flowrate and composition of the recycle stream, particularly hydrogen concentration, significantly influences the efficiency of turbo-expansion and the energy consumption of the process. The findings of this project aim to contribute valuable insights towards the development of efficient and cost-effective separation processes for the recovery of hydrocarbon.

8 REFERENCES

Alcañiz-Monge, J., Lozano-Castelló, D., Cazorla-Amorós, D., & Linares-Solano, A. (2009, August). Fundamentals of methane adsorption in microporous carbons. *Microporous and Mesoporous Materials*, *124*(1–3), 110–116. http://dx.doi.org/10.1016/j.micromeso.2009.04.041

Al-Qahtani, T., Karim, K., Bashir, M. A., & Al-Hammad, A. (2017, April 6). *Cryogenic separation of light olefins and methane from syngas* (WO 2017/056022 A1). WIPO. https://patents.google.com/patent/WO2017056022A1/en

Arc Energy. (2021, June 4). *Vessel Weight Calculator*. Retrieved December 17, 2022, from https://www.arcenergy.com/weightcalculator/

Aspen Technology, Inc. (n.d.). *Rate-Based Model of the CO2 Capture Process by TEA using Aspen Plus: V.86*.

Bancon, S., & Le Bec, R. (2007, December 18). *Syngas purification process* (US 7309378 B2). United States Patent and Trademark Office. https://patents.google.com/patent/US7309378?oq=US+7309378+B2

BASF Catalysts LLC. (n.d.). BASF 3A Molecular Sieve. In *BASF Catalysts* (BASF-9394 08/20). Retrieved December 12, 2022, from https://catalysts.basf.com/products/3a-molecular-sieve

Benyahia, F., & O'Neill, K. E. (2005). Enhanced Voidage Correlations for Packed Beds of Various Particle Shapes and Sizes. Particulate Science and Technology, 23(2), 169–177. https://doi.org/10.1080/02726350590922242

Brown, T., Kidnay, A., & Sloan, E. (1988). Vapor—liquid equilibria in the carbon dioxide-ethane system. *Fluid Phase Equilibria*, *40*(1–2), 169–184. http://dx.doi.org/10.1016/0378-3812(88)80028-1

Campbell, R. E., Wilkinson, J. D., & Hudson, H. M. (1995, October 29). *Hydrocarbon gas processing* (US5568737A). United States Patent and Trademark Office. https://patents.google.com/patent/US5568737A/en

Chandran, R., Leo, D. M., Freitas, S. R., Newport, D. G., Whitney, H. S. M., & Burciaga, Daniel. A. (2018, July 3). *Method for syngas clean-up of semi-volatile organic compounds with metal removal* (US 10011482 B2). U.S. Patent and Trademark Office. https://patents.google.com/patent/US10011482B2/en

Dalane, K., Dai, Z., Mogseth, G., Hillestad, M., & Deng, L. (2017, March). Potential applications of membrane separation for subsea natural gas processing: A review. *Journal of Natural Gas Science and Engineering*, *39*, 101–117. http://dx.doi.org/10.1016/j.jngse.2017.01.023

de Klerk, A. (2013). Fischer-Tropsch Process. *Kirk-Othmer Encyclopedia of Chemical Technology*. http://dx.doi.org/10.1002/0471238961.fiscdekl.a01

Demirel, Y., & Gerbaud, V. (2019). *Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical, Chemical and Biological Systems* (4th ed.) [Electronic (ScienceDirect)]. Elsevier. https://doi.org/10.1016/C2017-0-02734-9

Dow Inc. (2021). 2021 Environmental, social & governance report. In *Dow Corporate*. Retrieved April 5, 2023, from https://corporate.dow.com/content/dam/corp/documents/about/066-00397-01-2021-esg-report.pdf

Dow Inc. (2022). 2022 Notice of annual meeting of stockholders & proxy statement. In *Investors Dow*. Retrieved January 6, 2023, from https://s23.q4cdn.com/981382065/files/doc_financials/2021/ar/Dow_Inc_2022_Proxy_Statement.pdf#xd_co_f=M2EzYjY2MjktOTliZi00NTQ5LWJjZDMtNDlmYzZkMDdkN2Ew~

Ebrahimzadeh, E., Matagi, J., Fazlollahi, F., & Baxter, L. L. (2016, March). Alternative extractive distillation system for CO2–ethane azeotrope separation in enhanced oil recovery processes. *Applied Thermal Engineering*, *96*, 39–47. http://dx.doi.org/10.1016/j.applthermaleng.2015.11.082

Fang, H., & Duan, M. (2014). *Offshore Operation Facilities: Equipment and Procedures* [Electronic (ScienceDirect)]. Gulf Professional Publishing. http://dx.doi.org/10.1016/B978-0-12-396977-4.00003-2

Faramawy, S., Zaki, T., & Sakr, A. A. E. (2016, August). Natural gas origin, composition, and processing: A review. *Journal of Natural Gas Science and Engineering*, *34*, 34–54. https://doi.org/10.1016/j.jngse.2016.06.030

Faramawy, S., Zaki, T., & Sakr, A. E. (2016, August). Natural gas origin, composition, and processing: A review. *Journal of Natural Gas Science and Engineering*, *34*, 34–54. http://dx.doi.org/10.1016/j.jngse.2016.06.030

Ghasem, N. (2020). CO2 removal from natural gas. *Advances in Carbon Capture*, 479–501. https://doi.org/10.1016/b978-0-12-819657-1.00021-9

Hassan, T. N. A. T., Shariff, A. M., Pauzi, M. M. M., Khidzir, M. S., & Surmi, A. (2022, February 19). Insights on Cryogenic Distillation Technology for Simultaneous CO2 and H2S Removal for Sour Gas Fields. *Molecules*, *27*(4), 1424. http://dx.doi.org/10.3390/molecules27041424

He, X., Chen, D., Liang, Z., & Yang, F. (2022, March). Insight and Comparison of Energy-efficient Membrane Processes for CO2 Capture from Flue Gases in Power Plant and Energy-intensive Industry. *Carbon Capture Science & Technology*, *2*, 100020. https://doi.org/10.1016/j.ccst.2021.100020

Hongjun, Y., Shuanshi, F., Xuemei, L., Yanhong, W., & Jianghua, N. (2011). Economic Comparison of Three Gas Separation Technologies for CO2 Capture from Power Plant Flue Gas. *Chinese Journal of Chemical Engineering*, *19*(4), 615–620. https://doi.org/10.1016/S1004-9541(11)60031-1

Hu, H., Jiang, H., Jing, J., Pu, H., Tan, J., & Leng, N. (2018, November 28). Optimization and Exergy Analysis of Natural Gas Liquid Recovery Processes for the Maximization of Plant Profits. *Chemical Engineering & Technology*, *42*(1), 182–195. http://dx.doi.org/10.1002/ceat.201800238

IPCC, 2007: *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland, 104 pp.

Joule–Thomson effect. (n.d.). WikiDoc. Retrieved October 11, 2022, from https://www.wikidoc.org/index.php/Joule%E2%80%93Thomson_effect

Kertik, A., Wee, L. H., Pfannmöller, M., Bals, S., Martens, J. A., & Vankelecom, I. F. J. (2017). Highly selective gas separation membrane using in situ amorphised metal–organic frameworks. *Energy & Environmental Science*, *10*(11), 2342–2351. http://dx.doi.org/10.1039/c7ee01872j

Khol, A. L., & Nielsen, R. B. (1997). *Gas Purification* (5th ed.) [Electronic (ScienceDirect)]. Gulf Professional Publishing. https://doi.org/10.1016/B978-0-88415-220-0.X5000-9

Kim, J., Maiti, A., Lin, L. C., Stolaroff, J. K., Smit, B., & Aines, R. D. (2013, April 16). New materials for methane capture from dilute and medium-concentration sources. *Nature Communications*, *4*(1), 1–7. http://dx.doi.org/10.1038/ncomms2697

Korman, K. J., Decker, G. E., Dworzak, M. R., Deegan, M. M., Antonio, A. M., Taggart, G. A., & Bloch, E. D. (2020, August 13). Using Low-Pressure Methane Adsorption Isotherms for Higher-Throughput Screening of Methane Storage Materials. *ACS Applied Materials & Interfaces*, *12*(36), 40318–40327. http://dx.doi.org/10.1021/acsami.0c11200

Meng, F., Meng, Y., Ju, T., Han, S., Lin, L., & Jiang, J. (2022, October). Research progress of aqueous amine solution for CO2 capture: A review. *Renewable and Sustainable Energy Reviews*, *168*, 112902. http://dx.doi.org/10.1016/j.rser.2022.112902

Miller, B. (2010). *Clean Coal Engineering Technology* [Electronic (ScienceDirect)]. Butterworth-Heinemann. https://doi.org/10.1016/C2009-0-20236-4

Miller, B. (2015). *Fossil Fuel Emissions Control Technologies: Stationary Heat and Power Systems* [Electronic (ScienceDirect)]. Butterworth-Heinemann. https://doi.org/10.1016/C2014-0-00392-9

Mohan, S., & Katakojwala, R. (2021). The circular chemistry conceptual framework: A way forward to sustainability in industry 4.0. *Current Opinion in Green and Sustainable Chemistry*, *28*, 100434. https://doi.org/10.1016/j.cogsc.2020.100434

Mokhatab, S., Poe, W. A., & Mak, J. Y. (2015). *Handbook of Natural Gas Transmission and Processing: Principles and Practices* (3rd ed.) [Electronic (ScienceDirect)]. Gulf Professional Publishing. http://dx.doi.org/10.1016/B978-0-12-801499-8.00007-9

Molecular Sieve For Natural Gas Drying. (n.d.). Molecular Sieves Desiccants. Retrieved September 21, 2022, from https://www.molecularsievedesiccants.com/molecular-sieve-for-natural-gas-drying

Molecular sieve. (2012, August 9). WikiDoc. Retrieved September 13, 2022, from https://www.wikidoc.org/index.php/Molecular_sieve

Mollier Diagrams. (n.d.). Advanced Steam Traction. Retrieved October 12, 2022, from https://advanced-steam.org/5at/technical-terms/thermodynamics/mollier-diagrams/

Netusil, M., & Ditl, P. (2011, September). Comparison of three methods for natural gas dehydration. *Journal of Natural Gas Chemistry*, *20*(5), 471–476. http://dx.doi.org/10.1016/s1003-9953(10)60218-6

Nieskens, D. L. S., Ciftci, A., Groenendijk, P. E., Wielemaker, M. F., & Malek, A. (2017). Production of Light Hydrocarbons from Syngas Using a Hybrid Catalyst. *Industrial &Amp; Engineering Chemistry Research*, *56*(10), 2722–2732. https://doi.org/10.1021/acs.iecr.6b04643

Nieskens, D. L. S., Lunn, J. D., & Malek, A. (2018). Understanding the Enhanced Lifetime of SAPO-34 in a Direct Syngas-to-Hydrocarbons Process. *ACS Catalysis*, 9, 691-700. http://dx.doi.org/10.1021/acscatal.8b03465

Nonporous dense membranes. (n.d.). Big Chemical Encyclopedia. Retrieved October 13, 2022, from https://chempedia.info/info/nonporous_dense_membranes/

Nyce, G., Black, R., Czerpak, P., Faz, C., Freer, E., Harraz, H., Madgavkar, A., McCormick, J., Michalak, W., Patel, B., Radaelli, G., Rapold, T., Runnebaum, R., Scher, E. C., Zhang, A., Taheri, H., Rafique, H., Cizeron, J., Hong, J. K., & Schammel, W. (2015, July 16). *Ethylene-to-liquids systems and methods* (WO 2015/105911 A1). WIPO. https://patents.google.com/patent/WO2016205411A8/en

O'Rear, D. J. (2003, November 5). *Converting CO2 in natural gas to syngas using hydroge from naphtha reforming* (GB 2388118 A). UK Pattent Application. https://patents.google.com/patent/GB2388118A/en?oq=2388118

Oh, S. Y., Binns, M., Cho, H., & Kim, J. K. (2016, May). Energy minimization of MEA-based CO2 capture process. *Applied Energy*, *169*, 353–362. http://dx.doi.org/10.1016/j.apenergy.2016.02.046

Patterson, J. A. (1952). *Separation of ethane and ethylene by extractive distillation* (Patent No. 2610704). United States Patent Office. https://patents.google.com/patent/US2610704A/en

Pollefeyt, G., Santos, V. P., Yancey, D. F., Nieskens, D., Kirilin, A., & Malek, A. (2022). Direct Conversion of Syngas to Olefins over a Hybrid CrZn Mixed Oxide/SAPO-34 Catalyst: Incorporation of Dopants for Increased Olefin Yield Stability. *Industrial & Engineering Chemistry Research*, 61(46), 17001-17011. http://dx.doi.org/10.1021/acs.iecr.2c02511

Qazvini, O. T., Babarao, R., & Telfer, S. G. (2021, January 8). Selective capture of carbon dioxide from hydrocarbons using a metal-organic framework. *Nature Communications*, *12*(1). http://dx.doi.org/10.1038/s41467-020-20489-2

Rackley, S. A. (2010). *Carbon Capture and Storage* [Electronic (ScienceDirect)]. Butterworth-Heinemann. https://doi.org/10.1016/C2009-0-19306-6

Radaelli, G., Bridges, R., Rafique, H. A., Duggal, S., Vuddagiri, S., Cizeron, J., McCormick, J., Patel, B., & Lakhapatri, S. (2021, January 28). *Oxidative coupling of methane methods and systems* (US 2021/0024439 A1). United States Patent and Trademark Office. https://patents.google.com/patent/US20210024439A1/en

Radique, H. A., Vuddagiri, S., Harraz, H., Radaelli, G., Scher, E. C., McCormick, J., Iyer, R., Duggal, S., Cizeron, J., & Hong, J. K. (2015, July 16). *Oxidative coupling of methane impementations for olefin production* (WO 2015/106023 A1). WIPO. https://patents.google.com/patent/WO2015106023A1/en

Regufe, M. J., Tamajon, J., Ribeiro, A. M., Ferreira, A., Lee, U. H., Hwang, Y. K., Chang, J. S., Serre, C., Loureiro, J. M., & Rodrigues, A. E. (2015, June 22). Syngas Purification by Porous Amino-Functionalized Titanium Terephthalate MIL-125. *Energy & Fuels*, 29(7), 4654–4664. https://doi.org/10.1021/acs.energyfuels.5b00975

Riboldi, L., & Bolland, O. (2017, July). Overview on Pressure Swing Adsorption (PSA) as CO2 Capture Technology: State-of-the-Art, Limits and Potentials. *Energy Procedia*, *114*, 2390–2400. http://dx.doi.org/10.1016/j.egypro.2017.03.1385

Roumeliotis, I., & Mathioudakis, K. (2006, November). Analysis of moisture condensation during air expansion in turbines. *International Journal of Refrigeration*, *29*(7), 1092–1099. https://doi.org/10.1016/j.ijrefrig.2006.03.001

Santos, V. P., Pollefeyt, G., Yancey, D. F., Ciftci Sandikci, A., Vanchura, B., Nieskens, D. L., de Kok-Kleiberg, M., Kirilin, A., Chojecki, A., & Malek, A. (2020). Direct conversion of syngas to light olefins (C2–C3) over a tandem catalyst CrZn–SAPO-34: Tailoring activity and stability by varying the Cr/Zn ratio and calcination temperature. *Journal of Catalysis*, 381, 108-120. http://dx.doi.org/10.1016/j.jcat.2019.08.027

Santos, V., & Sabatino, P. (n.d.). Great start at Dow [Slides].

Schultes, M. (2003, January). Raschig Super-Ring: A New Fourth Generation Packing Offers New Advantages. *Chemical Engineering Research and Design*, *81*(1), 48–57. http://dx.doi.org/10.1205/026387603321158186

Singh, S. P., & Price, A. J. (2015, September 15). *Apparatus, systems, and processes for producing syngas and products therefrom* (US 9132402 B2). U.S. Patent and Trademark Office. https://patents.google.com/patent/US9132402B2/en

Soares. (2022). *Process Development Study of Primary Separation unit for Dow's novel Hybrid Catalyst Technology* [MThesis]. Instituto Superior Técnico, Lisboa.

Solution diffusion mechanism. (n.d.). Big Chemical Encyclopedia. Retrieved October 13, 2022, from https://chempedia.info/info/solution_diffusion_mechanism/

Steward, M. I., Jr. (2014). Design of Gas-Handling Systems and Facilities [Electronic (ScienceDirect)]. In *Surface Production Operations* (3rd ed., Vol. 2). Gulf Professional Publishing. https://doi.org/10.1016/C2009-0-64501-3

Tavan, Y., & Hosseini, S. H. (2013, November). A novel application of reactive absorption to break the CO2–ethane azeotrope with low energy requirement. *Energy Conversion and Management*, *75*, 407–417. http://dx.doi.org/10.1016/j.enconman.2013.06.015

Tavan, Y., Shahhosseini, S., & Hosseini, S. H. (2014a, February). Feed-splitting technique in the extractive distillation of CO2–ethane azeotropic process. *Separation and Purification Technology*, *122*, 47–53. http://dx.doi.org/10.1016/j.seppur.2013.10.041

Tavan, Y., Shahhosseini, S., & Hosseini, S. H. (2014b, June). Design and simulation of ethane recovery process in an extractive dividing wall column. *Journal of Cleaner Production*, *72*, 222–229. http://dx.doi.org/10.1016/j.jclepro.2014.03.015

Thacker, P. S. (2011, January 13). *Methods and system for separating carbon dioxide from syngas* (AU 2010202532 B2). Australian Patent Office. https://patents.google.com/patent/AU2010202532B2/en?oq=AU+2010202532+B2

The Different Types Of Recycling. (2021, September 7). Plastics for Change. Retrieved May 23, 2023, from https://www.plasticsforchange.org/blog/types-of-recycling

The Dow Chemical Company. (n.d.). *On our way to carbon neutrality: Dow Circles*. DowCircles.nl. Retrieved May 23, 2023, from https://dowcircles.nl/en/sustainability/roadmap-to-zero/our-way-to-carbon-neutrality

Torres-Ortega, C. E., Segovia-Hernández, J. G., Gómez-Castro, F. I., Hernández, S., Bonilla-Petriciolet, A., Rong, B. G., & Errico, M. (2013, December). Design, optimization and controllability of an alternative process based on extractive distillation for an ethane–carbon dioxide mixture. *Chemical Engineering and Processing: Process Intensification*, *74*, 55–68. http://dx.doi.org/10.1016/j.cep.2013.09.011

Tullo, A. H. (2022, July 24). *C&EN's Global Top 50 chemical firms for 2022*. C&EN (Chemical and Engineering News). Retrieved January 6, 2023, from https://cen.acs.org/business/finance/CENs-Global-Top-50-2022/100/i26

Zhang, S., Jiang, H., Jing, J., Qin, M., Chen, D., & Chen, C. (2020a, November). Comprehensive comparison of enhanced recycle split vapour processes for ethane recovery. *Energy Reports*, *6*, 1819–1837. http://dx.doi.org/10.1016/j.egyr.2020.07.010

Zhang, X., Song, Z., Gani, R., & Zhou, T. (2020b, January 13). Comparative Economic Analysis of Physical, Chemical, and Hybrid Absorption Processes for Carbon Capture. *Industrial & Engineering Chemistry Research*, *59*(5), 2005–2012. https://dx.doi.org/10.1021/acs.iecr.9b05510?ref=pdf

Zohuri, B. (2018). *Physiscs of Cryogenics: An Ultralow Temperature Phenomenon* [Electronic (ScienceDirect)]. Elsevier. https://doi.org/10.1016/C2017-0-01796-2

APPENDIXES

Appendix 1. Self-evaluation questionnaire

Table A1.1. Evaluation of acquired competences based on tasks performed by the student.

	Degree competences	Tasks performed that reflect the competences described	Self-evaluation [Rank 1 to 10]	Aspects to be improved
		Specific competences		
A1.1	Effectively apply knowledge of basic, scientific and technological materials pertaining to engineering.	Literature research, process modelling, process simulation and data analysis	10	N/A
A1.2	Design, execute and analyse experiments related to engineering	Process modelling & simulation and data analysis	8	Use of literature parameters to model the processes and accelerate process modelling tasks
A1.3	Be able to analyse and synthesize the continuous progress of products, processes, systems and services, whilst applying criteria of safety, economic viability, quality and environmental management. (G6)	Data analysis and report generation	9	Chose adequate calculation basis for experiment design (process modelling & simulation)
A1.4	Know how to establish and develop mathematical models by using the appropriate software in order to provide the scientific and technological basis for the design of new products, processes, systems and services and for the optimization of existing ones. (G5)	Process modelling & simulation	9	Use of literature parameters to model the processes and accelerate process modelling tasks
A2.1	Be able to apply the scientific method and the principles of engineering and economics to formulate and solve complex problems that arise in processes, equipment, installations and services, in which the material undergoes changes to its composition, state or energy content, these changes being characteristic of industrial chemistry and other related sectors such as pharmacology, biotechnology, materials sciences, energy, food and the environment. (G1)	Planification, literature research, process modelling, process simulation and data analysis	10	N/A
A2.2	Conceive, project, calculate and design processes, equipment, industrial installations and services in the field of chemical engineering and related industrial sectors in terms of quality, safety, economics, the rational and efficient use of natural resources and the conservation of the environment. (G2)	Process modelling & simulation	9	Use of literature parameters to model the processes and accelerate process modelling tasks
A2.3	Lead and technically and economically manage projects, installations, plants, companies and technological centres in the ambit of chemical engineering and related industrial sectors. (G3)	Planification & execution of the Master Thesis project	10	N/A
A3.1	Apply knowledge of mathematics, physics, chemistry, biology and other natural sciences by means of study, experience, practice and critical reasoning in order to establish economically viable solutions for technical problems (I1).	Process modelling, process simulation and data analysis	8	Gain a greater insight of the physical phenomena occurring in process equipment, correlate theoretical concepts with practical applications

Table A1.1. Evaluation of acquired competences based on tasks performed by the student. (cont.)

	Degree competences	Tasks performed that reflect the competences described	Self-evaluation [Rank 1 to 10]	Aspects to be improved
	Specific competences			
A3.2	Design and optimize products, processes, systems and services for the chemical industry on the basis of various areas of chemical engineering, including processes, transport, separation operations, and chemical, nuclear, electrochemical and biochemical reactions engineering (I2).	Process modelling & simulation	9	Use of literature parameters to model the processes and accelerate process modelling tasks
A3.3	Conceptualize engineering models and apply innovative problems solving methods and appropriate IT applications to the design, simulation, optimization and control of processes and systems (I3).	Process modelling & simulation	9	Use of literature parameters to model the processes and accelerate process modelling tasks
A3.4	Be able to solve unfamiliar and ill-defined problems by taking into account all possible solutions and selecting the most innovative. (I4)	Planification, literature research, process modelling, process simulation and data analysis	10	N/A
A3.5	Lead and supervise all types of installation, process, system and service in the different industrial areas related to chemical engineering (I5).	N/A	N/A	N/A
A3.6	Design, construct and implement methods, processes and installations for the integrated management of waste, solids, liquids and gases, whilst also taking into account the impacts and risks of these products (I6).	N/A	N/A	N/A
A4.1	Lead and organize companies and production and service systems by applying knowledge and abilities regarding industrial organization, commercial strategy, planning and logistics, mercantile and labour legislation, and financial and costs accounting (P1).	N/A	N/A	N/A
A4.2	Lead and manage the organization of work and human resources by applying criteria regarding industrial safety, quality management, occupation risk prevention, sustainability and environmental management (P2).	N/A	N/A	N/A
A4.3	Manage research, development and technological innovation whilst ensuring the transfer of technology and taking into account property and patent rights (P3).	Literature research, process modelling, process simulation, data analysis and elaboration of the Master Thesis report	10	N/A
A4.4	Adapt to structural changes in society caused by economic, energy or natural factors so as to be able to solve any resulting problems and to contribute technological solutions with a high commitment to sustainability (P4).	Execution of the Master Thesis project (tasks inside Dow's sustainability strategy)	9	Gain a greater insight of the industrial ecosystem, workflows and sustainability strategies
A4.5	Lead and monitor the control of installations, processes, products, certification, auditing, verification, testing and reports (P5).	N/A	N/A	N/A

Table A1.1. Evaluation of acquired competences based on tasks performed by the student. (cont.)

	Degree competences	Tasks performed that reflect the competences described	Self-evaluation [Rank 1 to 10]	Aspects to be improved
	Specific competences			
A5.1	Carry out, present and defend (once all the curriculum credits have been obtained) an original individually produced piece of work before a university panel. The work will consist of a professional integrated Chemical Engineering project that synthesizes (TFM1)	Planification & execution of the Master Thesis project	10	N/A
	Transversal competences			
B1.1	Communicate and discuss proposals and conclusions in a clear and unambiguous manner in specialized and non-specialized multilingual forums (G9).	Weekly meetings with company supervisor	10	N/A
B1.2	Adapt to changes and be able to apply new and advanced technologies and other important developments with initiative and entrepreneurial spirit. (G10)	Modification of the planification & execution plan of the project according to the feedback obtained in weekly meetings with company supervisor	9	Better track of the changes suggested by the supervisor.
B2.1	Lead and define multidisciplinary teams that are able to make technical changes and address management needs in national and international contexts. (G8)	N/A	N/A	N/A
B3.1	Work in a team with responsibilities shared among multidisciplinary, multilingual and multicultural teams	Execution of the Master Thesis project	10	N/A
B4.1	Be able to learn autonomously in order to maintain and improve the competences pertaining to chemical engineering that enable continuous professional development. (G11)	Planification & execution of the Master Thesis project	10	N/A
B5.1	Carry out and lead the appropriate research, design and development of engineering solutions in new or little understood areas, whilst applying criteria of creativity, originality, innovation and technology transfer. (G4)	Literature research, process modelling, process simulation, data analysis and elaboration of the Master Thesis report	10	N/A
B5.2	Bring together knowledge, make judgements and take decisions on the basis of incomplete or limited knowledge whilst taking into account the social and ethical responsibilities of professional practice. (G7)	Literature research, process modelling, process simulation, data analysis and elaboration of the Master Thesis report	10	N/A
	Nuclear competences			
C1.1	Have an intermediate mastery of a foreign language, preferably English	All social interactions carried out during the internship	10	N/A
C1.2	Be advanced users of the information and communication technologies	Literature research, process modelling, process simulation, data analysis and elaboration of the Master Thesis report	10	N/A
C1.3	Be able to manage information and knowledge	Literature research, data analysis and elaboration of the Master Thesis report	10	N/A

Table A1.1. Evaluation of acquired competences based on tasks performed by the student. (cont.)

	Degree competences	Tasks performed that reflect the competences described	Self-evaluation [Rank 1 to 10]	Aspects to be improved
	Nuclear competences			
C1.4	Be able to express themselves correctly both orally and in writing in one of the two official languages of the URV	Weekly meetings with company supervisor, final internship meeting with the whole team & elaboration of the Master Thesis report	10	N/A
C2.1	Be committed to ethics and social responsibility as citizens and professionals	Execution of the Master Thesis project (tasks inside Dow's sustainability strategy)	9	Gain a greater insight of the industrial ecosystem, workflows and sustainability strategies
C2.2	Be able to define and develop their academic and professional project	Planification & execution of the Master Thesis project	10	N/A

Table A1.2. Evaluation of the master thesis project and suggestion of improvements

Key steps	Evaluation [Rank 1 to 10]	Improvement proposed
Selection/assignment of the project (dissemination, communication, assignment requirements...)	10	Great project from a technical and a conceptual point of view. No improvements needed.
Stay (welcome, length, relationship, follow-up made by the company...)	10	Great stay at the company, very nice work environment and excellent follow-up made by company supervisor. No improvements needed.
Follow-up made by URV tutor	10	Excellent follow-up made by URV tutor. No improvements needed.
Other aspects to be considered (which ones...)	N/A	N/A

Appendix 2. Description of water removal technologies

Molecular sieves

Molecular sieve dryers are materials containing pores of a precise and uniform size. Molecules small enough to pass through the pores are physically adsorbed as a result of the forces existing at the surface of the material (*Molecular Sieve*, 2012). As the amount of water adsorbed is correlated to the surface available for adsorption, commercial adsorbents are materials with very large surface areas per unit weigh, usually in the form of granules or preformed shapes (Khol & Nielsen, 1997).

In petrochemical processes, sodium-based zeolites with cage sizes of 3 Å are commonly used for drying gases containing water. Aluminosilicates, silica gels, microporous charcoals or other zeolites may also be used as molecular sieves (*Molecular Sieve*, 2012; Singh & Price, 2015).

The adsorption mechanism is explained by Langmuir model. Sites of residual valency exist on the surface of adsorbents. When a water molecule from the gas collides with an unoccupied site, it remains attached. The adsorbed molecule may leave the surface, but other water molecules will continually adhere. When adsorption is started, many active sites exist and the number of molecules adhering exceeds the number of those leaving the surface. As the surface becomes covered, the probability of a water molecule in the gas finding an unoccupied space decreases, until finally the rate of adhesion equals the rate of deadhesion, which represents the condition of equilibrium. At that point, the bed has become loaded with water and must then either be discarded, removed for reclaiming or regenerated in place (Khol & Nielsen, 1997).

PTSA technology is used to gain the maximum efficiency by regenerating the beds. For this cyclic operation, a minimum of two desiccants beds are used: typically, one bed dries the gas while the other is being regenerated (*Molecular Sieve for Natural Gas Drying*, n.d.; Netusil & Ditl, 2011). Additional beds can be used to increase the capacity of the unit or to continue with the operation in case of malfunction of one of the beds. Back-up beds are especially important because dehydration is usually an important operation in a process: if the dehydration section fails, the whole process must be stopped to avoid operational and safety issues.

PSA cycles use pressure reductions to regenerate the adsorbent. When the total pressure decreases, so does the partial pressure of adsorbate, leading to desorption (Khol & Nielsen, 1997).

One of the typical procedures for PSA described by Rackley (2010) is explained below with the support of Figure A2.1.

1. The bed is fed at high pressure with the gas to be dehydrated. Water is adsorbed and the rest of gas is recovered (light product).
2. The bed is regenerated by applying co-current depressurization to a medium pressure.
3. A counter-current depressurization to a low pressure is applied. Water (heavy product) starts to be recovered.
4. Light product is refluxed to the bed to further clean it from the heavy product.
5. Light product is refluxed to the bed at high pressure to improve the purity of the light product of the next cycle.

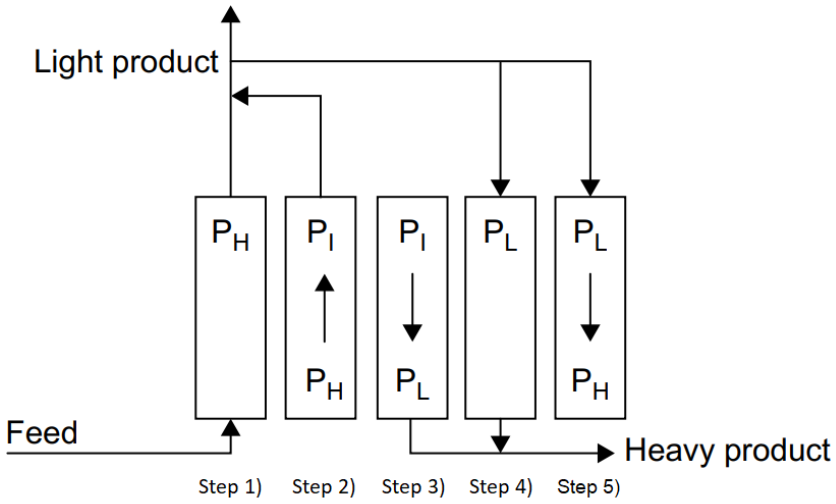

Figure A2.1. Scheme of a PSA cycle. Source: Rackley (2010), modified.

Other configurations can be used, as the optimization of PSA cycles is an active area of research. Further information about other designs is found in the literature (Chandran et al., 2018).

TSA cycles use temperature increments to regenerate the adsorbent. When the temperature is raised, adsorbed molecules are stimulated and desorbed (Khol & Nielsen, 1997). Heating can be provided as an ordinary burner, as a shell and tube exchanger warmed by steam or hot oil, or by the own regenerating gas (Netusil & Ditl, 2011). An alternative to TSA is electric swing adsorption, which uses Joule effect to achieve a faster heating (Miller, 2014; Rackley, 2010).

Although PSA can be used in the industry, TSA is usually selected because the working capacity of the catalyst is more dependent on temperature than on pressure. For applications with significant differences in pressure, PSA can also be selected.

Although PTSA cyclic operations allow the regeneration of beds in continuous processes, they imply higher capital and operating costs compared to other alternatives (Dalane et al., 2017).

To calculate its energetic requirements, Netusil & Ditl (2011) use a 10^5 Nm^3/h saturated stream of natural gas at 30 °C (approximately 1000 ppmv of water) which concentration must be reduced to the equivalent to the gas at –10 °C and 4 MPa (approximately 85 ppmv of water). The software *Aspen Plus V11* has been used to determine the equivalent water mass flow removed studied by the authors. *SRK* thermodynamic model has been chosen for the simulation. A pressure of 7 MPa has been studied, as it is the minimal studied by the authors, and a natural gas of the composition described in Table A2.1 has been used.

The simulation provides a value of approximately 8.5 kg/s of water removed. The results of Netusil & Ditl (2011) show that for the studied technology operating at 7 MPa, a power of 235 kW is needed. Therefore, the energy requirement for this technology is approximately 27.5 kJ/kg water removed.

Table A2.1. Natural gas composition used to determine the water removed in Netusil & Ditl (2011)

Species	Molar fraction (%)
Methane	93.07
Ethane	3.70
Propane	0.90
Isobutane	0.29
N-butane	0.13
Isopentane	0.07
N-hexane	0.07
Carbon dioxide	1.10
Nitrogen	0.68

Despite higher costs when compared to other alternatives, concentrations lower than 1 ppmv can be achieved, making this technology useful for applications where extremely low levels of water are required (Netusil & Ditl, 2011). It is worth highlighting its high tolerance for changes, its robustness, its reliable operation and its long history of commercial application.

Some of the main operational problems of PTSA are its non-steady state run and fouling by the formation of green oil from the oligomerization of light olefins (Dalane et al., 2017; Netusil & Ditl, 2011). Green oil formation has been mitigated to some extent with the most recent advances in the adsorbent catalysts.

Glycol absorption

Glycols are solvents with a high affinity for water. They are non-corrosive and non-toxic, do not react with short-chain hydrocarbons, and have a low vapor pressure and a high thermal stability. Triethylene glycol (TEG) is usually chosen among other glycols for its high boiling point (decreasing vaporization loss and operating costs) and for its high decomposition temperature (Dalane et al., 2017).

The basic glycol absorption process according to Khol & Nielsen (1997) and Netusil & Ditl (2011) is described below with the support of Figure A2.2.

1. Liquid hydrocarbons and free water are removed in a scrubber, as any entrainment results in fouling or foaming (Mokhatab & Mak, 2014).
2. Feed gas is fed to the bottom of the glycol contactor (either a trayed or a packed bed column).
3. Concentrated glycol is fed to the top of the glycol contactor and absorbs water from the gas while flowing downward through the column.
4. Dried gas leaves the top of the contactor and is used to cool the glycol feed. It may then pass through a scrubber which removes entrained glycol droplets.

5. Rich glycol flows out the bottom of the contactor and is used to provide cooling and condense water vapor at the top of the still column. This raises the temperature of the enriched solvent, which may be further heated by heat exchange with the hot lean glycol before or after flashing.
6. The solvent enters a flash drum where dissolved hydrocarbon gases are released and recovered.
7. After flashing, TEG solution is filtered and sprayed into the still column (either trayed or packed).
8. Water is stripped out of the glycol and the regenerated solvent is then cooled and pumped back to the glycol contactor column.

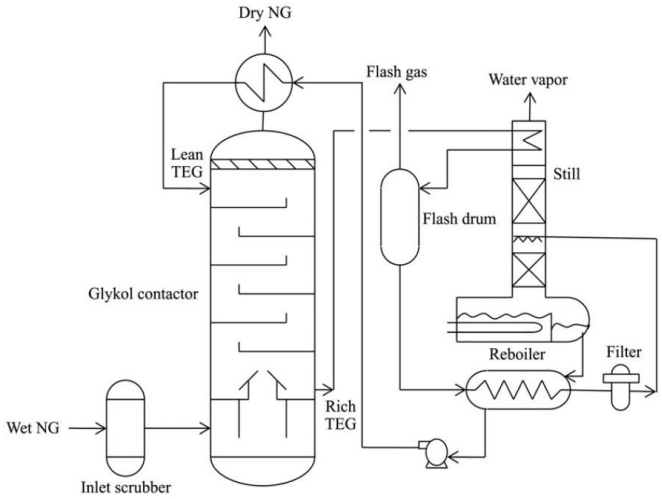

Figure A2.2. Scheme of absorption dehydration. Source: Netusil & Ditl, 2011.

The significant difference in the boiling points of glycol and water results in a very effective separation that can be achieved with few separation stages. By condensing a portion of the overhead vapor, a water reflux to provide rectification is obtained and glycol losses caused by entrainment are avoided. Heat for the distillation is provided by a direct fired reboiler (Khol & Nielsen, 1997).

Gas stripping can be implemented to enhance TEG regeneration. Drizo® & Coldfinger® are alternatives to the traditional stripping gas units (Netusil & Ditl, 2011).

Glycol absorption provides a high recovery of water at low capital costs (2 – 3 times lower than molecular sieves) and at medium-low operating costs (approximately 13 kJ/kg water removed, according to the calculations already described in the previous section), as reported by Netusil & Ditl (2011).

One of the challenges of this technology is the contamination of the glycol solution. Although short-chain hydrocarbons are not absorbed, heavier hydrocarbons and oxygenated species such as methanol or DME may be retained in the solvent. Even trace concentrations in the gas may result in buildup, that can cause foaming or degradation into “black mud” (Netusil & Ditl, 2011).

Entrainment of glycols to the process is also a serious operational problem, as it can cause fouling or undesired reactions in other separation units or in the product work-up units.

Condensation by Joule-Thomson effect cooling or isentropic expansion cooling

Condensation is applied for simultaneous dehydration of gas and hydrocarbons recovery. These technologies are based on the expansion of a gas to reduce its temperature: if it is lower or equal to the saturation temperature at the new pressure, a partial condensation takes place.

Isenthalpic free expansion is performed using a throttling device that must be well insulated to avoid the absorption of energy from the surroundings. For this reason, this phenomenon is sometimes referred as adiabatic expansion. Note that during an isenthalpic expansion, entropy of the system varies. When conditions favor partial condensation, a knockout drum is used for phase separation. For a better understanding of these favorable conditions for condensation, assume supercritical steam at 40 MPa and 600 ºC (red mark on Figure A2.3, in page 104). An isenthalpic expansion decreases the steam temperature (the higher the pressure drop, the lower the temperature achieved), but it can never lead to steam condensation. Assume now steam at 60 MPa and 500 ºC (green mark on Figure A2.3). In this case, an isenthalpic expansion not only decreases the steam temperature, but also leads to partial condensation.

Isentropic expansion is performed in a gas turbine, that must be well insulated to avoid the absorption of energy from the surroundings. The main difference compared to isenthalpic expansion is that entropy of the system is maintained constant. For this purpose, the system is assumed adiabatic and reversible (that is, the work applied to the turbine is frictionless). When conditions favor partial condensation, a knockout drum is used for phase separation. For a better understanding of these favorable conditions for condensation, assume steam at 1 MPa and 800 ºC (purple mark on Figure A2.3). An isentropic expansion decreases the steam temperature (the higher the pressure drop, the lower the temperature achieved), but it can never lead to steam condensation. Assume now steam at 40 MPa and 500 ºC (orange mark in Figure A2.3). In this case, an isentropic expansion not only decreases the steam temperature, but also leads to partial condensation.

Two physical mechanisms rule the isenthalpic expansion of gases. In the first mechanism, as the gas expands, the average distance between molecules grows. Because of intermolecular attractive forces, expansion causes an increase in the potential energy of the gas. If no external work is extracted and no heat is transferred, the total energy of the gas remains the same and the increase of potential energy causes a decrease in kinetic energy and, therefore, in temperature. In the second mechanism, during gas molecule collisions, kinetic energy is temporally converted into potential energy. As the average intermolecular distance increases, there is a drop in the number of collisions per time unit, which causes a decrease in the average potential energy. As total energy is conserved, this leads to an increase in kinetic energy (*Joule–Thomson Effect*, n.d.).

Below a certain temperature called “inversion temperature”, the first mechanism dominates, and an isenthalpic expansion causes a temperature drop. This is the case of most real gases at the usual working temperatures and pressures. Above the inversion temperature, the second mechanism dominates, and expansion heats up the gas. This is the case of gases like hydrogen, helium or neon at ambient temperature and atmospheric pressure; although other real gases also experience this phenomenon at very high pressures. Back to Figure A2.3, assume supercritical steam at 1000 MPa and 400 ºC (yellow mark). An isenthalpic expansion down to 300 MPa increases the temperature up to 500 ºC. That is why the presence of H_2 in syngas may substantially decrease the temperature drop (Radique et al., 2015).

In the case of isentropic adiabatic expansion, vapor is applying a positive work towards the turbine during the expansion, reducing the internal energy of the gas and, therefore, its temperature. For this phenomenon, there is no inversion temperature effect, and the temperature of the gas always decreases. For the same reason, the presence of hydrogen in the system is not expected to decrease the temperature drop.

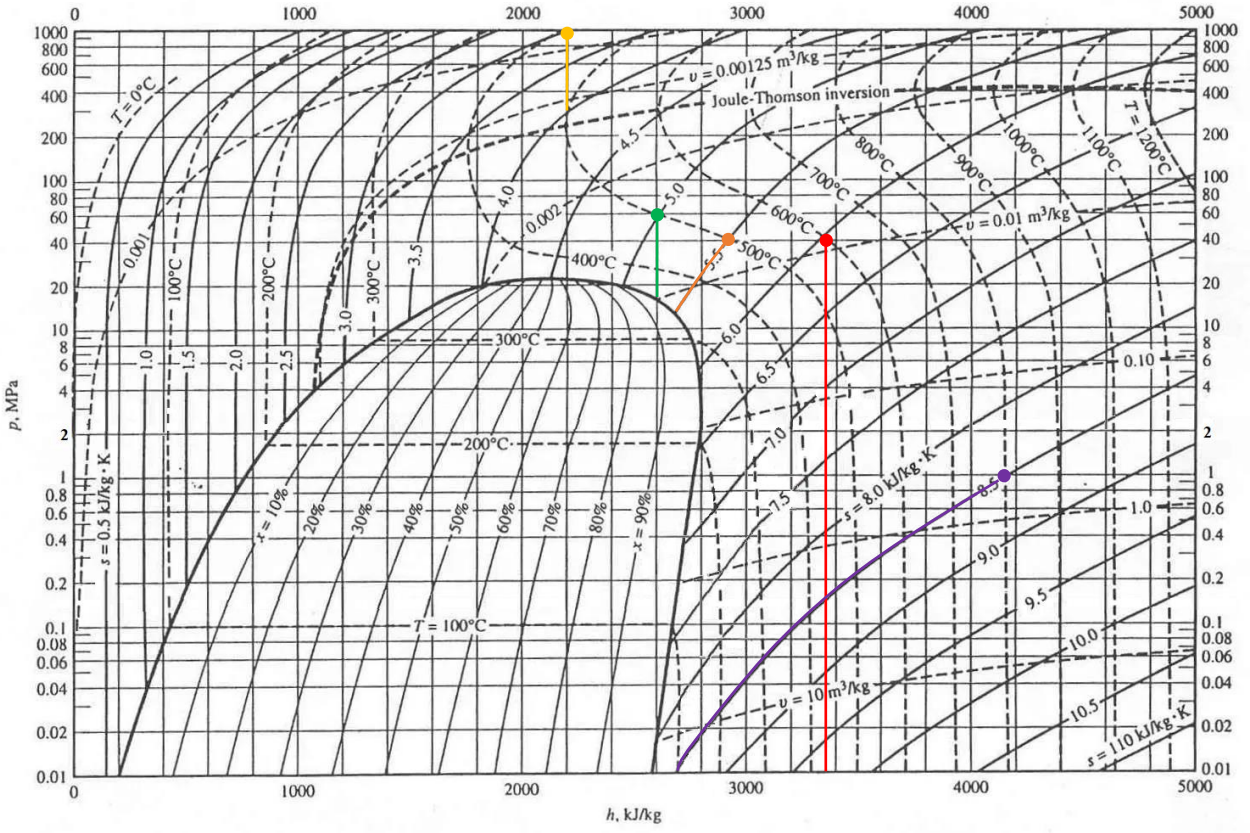

Figure A2.3. Water enthalpy-pressure diagram. Source: Mollier Diagrams, n.d. (modified).

Netusil & Ditl (2011) describe one of the typical procedures for JT–based dehydration, explained below with the support of Figure A2.4. For isentropic expansion, the throttling valve is replaced by a turbine.

1. Wet gas is fed to an air cooler. In cases when JT cooling is insufficient (e.g., the usable pressure drop is insufficient), this pre-cooler may be needed.
2. The gas is throttled and the lower temperature cause by the JT effect leads to partial condensation of steam.
3. The stream in vapor-liquid equilibrium is fed inside the knockout drum. The droplets created are removed from the gas stream by a demister inside the vessel. If the usable pressure difference is large, JT effect is so strong that internal heating of the drum is required to defreeze any ice that may form.
4. Condensate is removed from the system.

5. Vapors after the first flash are directed to a second heat exchanger, where vapor is pre-cooled using the cold vapor from the second knockout drum.
6. Vapors enter a second external cooler. If the cooling effect of JT effect is poor, this cooler is turned on.
7. Steps 2, 3 and 4 are repeated for the expansion.
8. Dry gas is used to pre-cool the vapors fed to the second knockout drum.

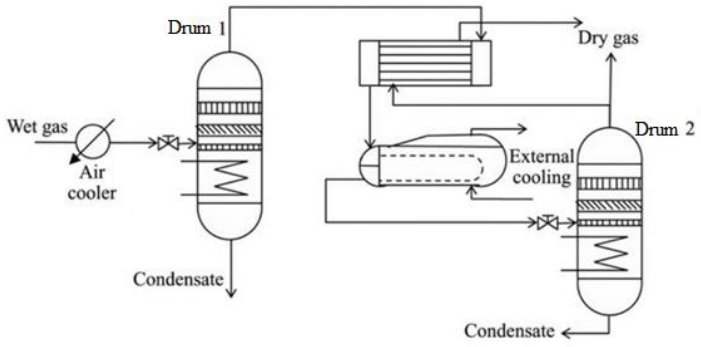

Figure A2.4. Scheme for dehydration using JT. Source: Netusil & Ditl, 2011 (modified).

As there is only a partial recovery of water, this technology can be used for bulk water removal prior to other refining dehydration units. Condensation has no selectivity for water (as once the stream reaches the dew point, it depends only on the vapor-liquid equilibrium of the mixture), but hydrocarbons are easily recovered from water.

Capital costs are reduced to the knockout drums and the expansion valves for isenthalpic expansion and to the same vessels and the turbines for isentropic expansion. When large pressure drops are allowed, there is no need for external refrigeration and the energy demand is minimal. When additional cooling is required, refrigeration significantly increase the energetic requirements of the operation, potentially making this technology unviable.

Isentropic expansion avoids inversion temperature issues, but the capital cost of turbines is significantly higher than that of throttling valves. However, for large pressure drops or cryogenic temperatures, throttling valves are not adequate and the use of turboexpanders may be considered.

Retrograde behavior of the mixture can lead to safety risks if not considered. For binary mixtures, a temperature decrease of a saturated vapor always results on a decrease of pressure. However, multicomponent mixtures have complex behaviors and the pressure may increase for a temperature drop. Figure A2.5 compares the result of a temperature reduction for a binary mixture with that for a multicomponent mixture.

Attention should be paid to the formation of methane hydrate. This phenomenon is favored at very high pressures and low temperatures, and is usually prevented by injecting methanol or monoethylene glycol hydrate inhibitors (Mokhatab & Mak, 2014; Netusil & Ditl, 2011). At the operating pressures of this process, methane hydrate is highly unlikely to be formed.

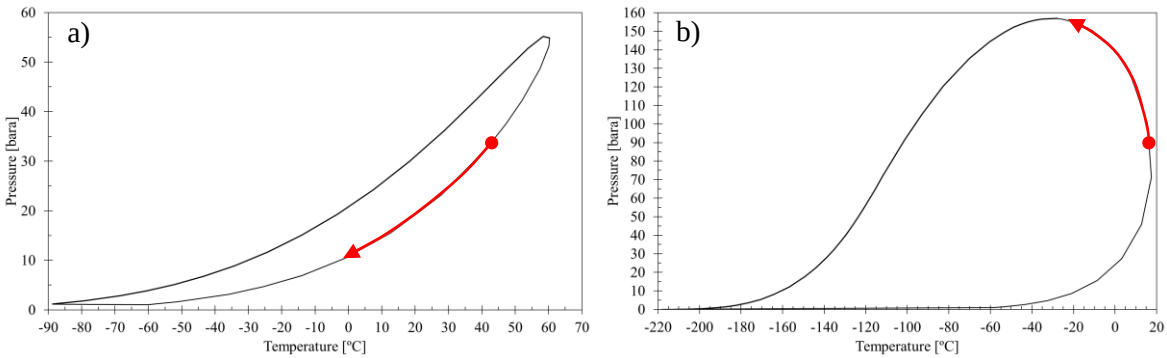

Figure A2.5. PT phase diagram for a) a binary mixture of 50 % of ethylene and 50 % of propylene (molar) and b) a multicomponent mixture with retrograde behavior of approximately 28.5 % CO, 13.5 % CO_2, 22.5 % CH_4, 8 % ethane, 9.5 % propane, 2 % butane, 0.3 % pentane, 0.4 % ethylene, 1.3 % propylene and 1.4 % nitrogen (molar). Data obtained using Aspen (PENG-ROB). Red arrows show the effect of a decrease of temperature for a given initial P and T.

Membranes

Dalane et al. (2017) suggest membrane separation for natural gas dehydration.

Technologies described are mostly based on dense non-porous membranes. These consist of a dense film to which gases are soluble to a certain extent. Due to a concentration gradient, the absorbed species diffuse through the matrix and are desorbed on the permeate side. This mechanism is known as solution-diffusion and allows the separation of species of similar size if their diffusivity and solubility differ significantly. Although high selectivity is reached, permeability is typically quite low in comparison with porous membranes (*Nonporous Dense Membranes*, n.d.; *Solution Diffusion Mechanism*, n.d.).

Polydimethylsiloxane, poly(phenylene oxide), cellulose acetate, Pebax® and Nafion™ are materials studied for this application as a result of their extremely high water permeability and their good water/methane selectivity according to Dalane et al. (2017).

The authors explain that membranes do not need solvents to operate, do not have direct emissions into the atmosphere, allow easy extensions due to their compactness and lightness, and have an overall smaller footprint compared with other traditional dehydration technologies. However, one of their main drawbacks is the high pressure ratio retentate-permeate required for streams with low concentrations of water when high purity permeates are required. Therefore, the viability of this technology in an industrial scenario depends mainly in the pressure drop available.

To overcome this challenge, membrane absorbers (e.g., TEG) in combination with solvent regeneration can be considered; but very little research has been conducted and high operating pressures are still needed (Dalane et al., 2017).

Some studies suggest that membrane systems can be competitive for small to medium-scale plants and gives examples of semi-commercial natural gas dehydration systems that use membranes (Dalane et al., 2017); but in practice few studies have been found in the literature using membrane dehydration for a stream with a similar composition to the one at the outlet of the syngas conversion reactor.

Appendix 3. Description of carbon dioxide recovery technologies

Amine washes

Chemical absorption is the preferred technology for high concentrations of CO_2 and when high removal rates are required (Bancon & Le Bec, 2007).

Absorption occurs when CO_2 molecules enter the bulk phase of the solvent. Carbon dioxide reacts with some of the absorbing substances, enhancing mass transfer between the gas and the liquid phase and "capturing" CO_2.

The absorption unit can use an aqueous solution of various alkylamines such as mono-, di- and triethanolamine (TEA), methyldiethanolamine, activated methyldiethanolamine, diglycolamine or diisopropanolamine. When the use of amines is undesirable, caustic-based wash systems using aqueous solutions of alkali carbonate-based compounds with little or no amines can be used (Miller, 2014; O'Rear, 2003; Radique et al., 2015; Singh & Price, 2015).

Alkali carbonate-based solvents have a higher overall capacity for CO_2 absorption, as the saturation pressure of CO_2 at the top of the column is lower for alkali carbonate-based solvents compared to amine systems. These solvents are very cheap, so they are typically not regenerated but disposed. However, as very high pH is obtained, equipment made of special alloys or passivated must be used to avoid corrosion, increasing dramatically the capital cost.

For the carbon dioxide to react with the amine or alkali carbonate-based solvents, it must first be physically absorbed in the liquid phase. This vapor-liquid equilibrium depends on factors such as pressure, temperature and surface area.

The chemical absorption mechanism of CO_2 is complex and changes with the absorbent used. To illustrate the reaction system of a common amine wash system, an example using TEA is given. To model the system, electrolyte solution chemistry must be used. The following mechanism is suggested by Aspen Technology, Inc, n.d.:

$$2H_2O \leftrightarrow H_3O^+ + OH^-$$

$$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$$

$$TEA + H_3O^+ \leftrightarrow H_2O + TEAH^+$$

$$TEAH^+ + HCO_3^- \leftrightarrow TEA + H_2O + CO_2$$

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$HCO_3^- \rightarrow CO_2 + OH^-$$

A basic amine wash process is summarized below with the support of Figure A3.1.

1. Gas to be treated is fed to the bottom of the absorber.
2. Semi-lean amine is fed to the column for bulk carbon dioxide removal. Lean amine is fed for CO_2 rectification. The amine-based solvent absorbs and reacts with carbon dioxide from the gas while flowing downward through the column.

3. Water is fed to the top of the column to absorb entrained amines from the gas. Alternatively, the purified gas can pass through a scrubber using, for example, a sodium hydroxide solution.
4. Rich amine flows out the bottom of the absorber and is used to provide cooling to the lean amine stream. The rich amine is heated to favor carbon dioxide desorption.
5. The rich solvent is fed to a flash tank, decreasing the pressure to partially desorb CO_2 from the solvent. A pressurized carbon dioxide stream is obtained (decreasing energy consumption of subsequent compression).
6. The rich amine is fed to the stripper column at low pressure, where the solution is regenerated. A stream is extracted from the column in a given stage above the reboiler, decreasing the duty of the column. The stream is pumped back to the absorber column as semi-lean solvent.
7. A stream is extracted from the bottom of the column, fully regenerated, and is pumped back to the absorber column as lean solvent.
8. Water condensate is fed to the top of the column to absorb entrained amines from the CO_2. Carbon dioxide at low pressure is obtained at the top of the column.

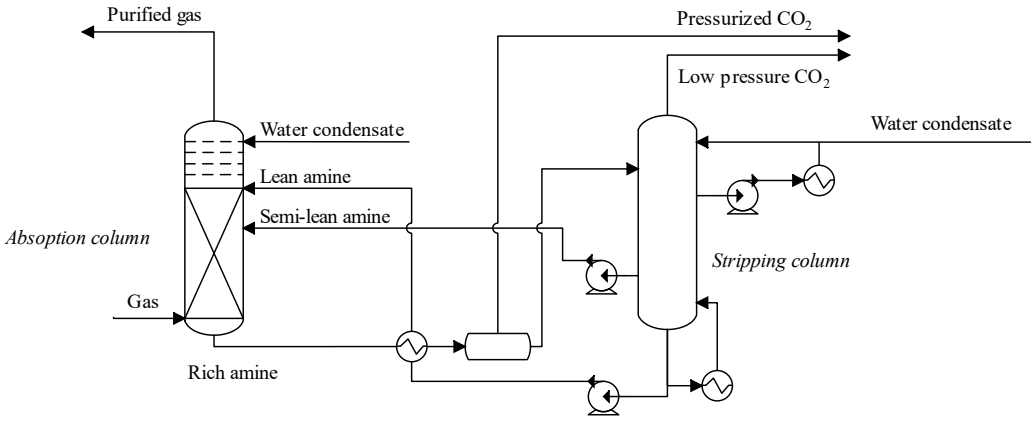

Figure A3.1. Scheme of a generic amine-based CO_2 absorber.

This design is based on bulk removal of CO_2 in the absorber using a semi-lean stream only partially regenerated. Only a small fraction of the flow is directed to the regenerator, and this fully regenerated lean stream is used only for polishing the last small amount of CO_2 in the top section of the absorber column. The idea is to minimize the energy consumption of the regeneration by reducing the amount of solvent actually regenerated and increasing the overall circulation rate.

As most of the solvent is not completely regenerated and the desorption of CO_2 is mostly caused by the vapor-liquid equilibrium for the semi-lean solvent, most part of CO_2 absorption is physical (using the semi-lean solvent).

In the absorption column, high carbon dioxide partial pressures are required to increase the concentration of CO_2 in the liquid phase. Temperature must reach a compromise between reaction kinetics and physisorption equilibrium.

In the stripping column, low pressures are needed to decrease the concentration of carbon dioxide in the liquid phase and shift the equilibrium reaction towards the chemical desorption of CO_2. High temperatures favor both kinetics and physical desorption, but special care must be taken to avoid the degradation of the amine solvent.

The first column is based on a random packing filling for the absorption section and a trayed configuration for the water wash section. By using random packing, a high contact area between the liquid and the gas phase is achieved. By using trays, a liquid loading able to absorb entrained amines is achieved.

Chemical absorption provides high CO_2 recovery and has a high selectivity for carbon dioxide. The maturity of this technology makes it one of the preferred methods in the industry for carbon dioxide capture (Meng et al., 2022). The operation costs for this technology depend on the concentration of CO_2 in the stream to be treated and on the concentration of CO_2 that must be reached.

To calculate its operational and capital costs, Zhang et al. (2020b) use a 1 kmol/s stream of syngas of a given composition at 40 °C and 1 bar with a concentration of CO_2 of 25 $\%_{mol}$, reducing it to 1 $\%_{mol}$. That is approximately 7.3 kg/s of CO_2 removed. Authors' results show a process total annualized cost of 18 M$/year (summation of annualized capital cost and operating cost). Therefore, the relative total cost is $78 \cdot 10^{-3}$ $/kg CO_2 removed. Regarding the concentration of CO_2 in the stream to be treated, the total annualized cost increases steeply for higher concentrations of carbon dioxide. For the concentration of CO_2 that must be reached, experience shows that the energetic requirements of this technology increase linearly when very low concentrations are needed.

One of the challenges of this technology is the contamination of the amine solution, as even trace concentrations can build up and cause foaming and degradation of the solvent. Other operational problems are entrainment of the amine solution that could cause severe corrosion problems downstream, or the corrosion of the own amine wash equipment due to the low pH reached (Meng et al., 2022).

Selexol® & Rectisol®

Selexol® and Rectisol are physical absorption commercial technologies.

Selexol® process uses dimethyl ethers of polyethylene glycol (DMPEG) as absorbent, but diisopropanolamine can be added to increase the carbon captured in the process. The process operates at relatively high pressure and mild temperatures, offering reduced costs by minimizing refrigeration duty. It can reduce CO_2 levels up to 85 % (Miller, 2014; Steward, 2014).

Rectisol process uses methanol as physical solvent, achieving higher absorption rates of a wider range of species. However, the operating temperature is lower than in Selexol®, increasing the refrigeration duty (Miller, 2014; Rackley, 2010; Steward, 2014).

Conceptually, the operation is very similar to the glycol absorption. The basic glycol absorption process is described in *Appendix 2. Description of water removal technologies*.

Physical absorption technologies provide high recovery rates, but the selectivity of CO_2 is relatively low. Rackley (2010) reports that solubilities of propane and other hydrocarbons in DMPEG are usually higher than the solubility of CO_2, and the removal rate of these hydrocarbons from the gas stream will depend on the process operating conditions.

The operation costs for this technology depend on the concentration of CO_2 in the stream to be treated, on the concentration of CO_2 that must be reached and on the operation pressure. Using the same conditions of the previous section, Zhang et al. (2020b) estimate a total annualized cost of 24 M$/year. Therefore, the relative total cost is $104 \cdot 10^{-3}$ $/kg CO_2 removed. Regarding the concentration of CO_2 in the stream to be treated, the total annualized cost increases mildly for higher concentrations of carbon dioxide. For the concentration of CO_2 that must be reached, experience shows that the energetic requirements of this technology increase exponentially when very low concentrations are needed.

One of the challenges that this technology is the contamination of the absorbent solution. Literature shows that the DMPEG is not selective to CO_2, so buildup, foaming and degradation are expected. Entrainment of glycol to the process is also a serious operational problem, as it can cause fouling or undesired reactions in other separation units or in the product work-up units.

Other technologies applied only in low TRL are improved amine-based systems and ionic liquid solvents (Rackley, 2010).

Molecular sieves

PTSA is a widely reported technique used to capture CO_2. Its main characteristics have already been described in *Appendix 2. Description of water removal technologies*.

Sodium-based zeolites have a pore size too small for the capture of carbon dioxide, so potassium-based zeolites with pore sizes of 4 – 5 Å are used.

The selectivity towards CO_2 is dependent on the technology used. Typical physisorbents show a preference for unsaturated hydrocarbons over CO_2, making this technology unsuitable. Novel adsorbents can increase the selectivity for carbon dioxide, but these materials are still at low TRL (Qazvini et al., 2021). Hassan et al. (2022) describe that the efficiency of the adsorption column decreases with a high number of regeneration cycles.

Membranes

The use of membranes for the separation of carbon dioxide is widely reported in the literature.

Some of the materials with a higher potential use in CO_2 capture are cellulose acetate or triacetate membranes and polyamide membranes (Dalane et al., 2017).

Commercial technologies such as Cynara/NATCO's or Separex from UOP-Honeywell are proved to achieve pipeline specifications for low volumetric flows and low carbon dioxide content to be removed; but fail to achieve specifications for larger flows or larger amounts of CO_2 removed. Technologies with improved performance are still limited to the laboratory scale (Dalane et al., 2017; Rackley, 2010).

Rackley (2010) describes polymeric membranes as a suitable option to separate ethane from CO_2, due to the problematic caused by the azeotrope formed between these two species. In this case, the carbon dioxide content of the stream is much higher and some of the problems mentioned could be fixed. In addition to the advantages already mentioned in *4.2 Water removal*, membranes can tolerate variations in the concentration of CO_2 in the feed stream (Dalane et al., 2017).

However, there are some inherent problems in membrane systems. The same authors describe as one of the main issues the presence of contaminants in the stream, as particles and other viscous substances can block membrane pores. Other contaminants are water vapor, that causes swelling and hence changes in the membrane performance; and higher hydrocarbons, that can decrease the membrane permeation ratio as the hydrocarbons slowly coat the membrane surface. The last can also cause plasticization of the membrane, a process whereby penetrant dissolution within the polymer matrix causes membrane swelling or dilatation. This process usually results in an increase permeability, but a reduced selectivity. An appropriate pre-treatment of the membrane can reduce this phenomenon.

Given the large amount of gas to be processed and the low concentration of carbon dioxide in the feed, very large surface areas or very high transmembrane pressures are required, making the capital or the operating and energetic costs too high (Hongjun et al., 2011; Meng et al., 2022; Miller, 2014). Other authors like Dalane et al. (2017) indicate that if large pressure drops are available (as it is in the case of natural gas sweetening), energetic requirements of membrane technologies are relatively low compared with alternative technologies.

Some alternatives that are able to deal with some of the challenges described are facilitated transport membranes (FTMs), inorganic membranes, mixed-matrix membranes (MMMs) and membrane contactors.

FTMs contain reactive carriers in their selective layers, enhancing the transport of gas through the membrane by the reversible reactions between carriers and carbon dioxide. This allows facilitated diffusion in addition to the solution-diffusion transport mechanism. FTMs can be in the form of support liquid membranes, ion-exchange membranes or fixed-site-carrier membranes (although mobile carriers give higher permeability and selectivity than fixed carriers). For hydrophilic FTMs, the humidity level of the feed gas is important to maintain a high performance, as water vapor can swell the membrane, increase the mobility of the carriers and accelerate CO_2 transport. Although FTMs are stable, evaporation of carrier can gradually reduce the membrane separation performance over time. Moreover, the partial pressure of CO_2 still affects the performance of this technology, as high partial pressures cause carrier saturation and lead to a decline in permeability and selectivity (Dalane et al., 2017).

Inorganic membranes have higher selectivity and permeability compared to polymeric membranes, as well as an excellent resistance to harsh environments, high temperatures and high pressures. The most studied inorganic membranes are carbon molecular sieves, zeolite membranes (SAPO-34, DDR-type, etc.) and metallic membranes. Their industrial application is still limited due to their high fabrication costs and difficulties in large-scale fabrication. Additionally, inorganic membranes based on molecular sieving usually suffer huge performance drops or even the loss of functions due to the competitive sorption of impurities, especially water, into the micro-pores (Dalane et al., 2017).

Mixed-matrix membranes combine the advantages of polymeric membranes and of inorganic membranes, as they are made of a bulk continuous polymer phase and of a dispersed inorganic particle phase. MMMs achieve higher selectivity and permeabilities than polymeric membranes, while avoiding the fragility inherent in inorganic membranes. Various inorganic fillers can be used; as for example zeolites, carbon molecular sieves, silica, metal-organic frameworks, and carbon nanotubes. Inorganic fillers change the polymer packing and increase the free volume, increasing gas diffusion through the membrane. Fillers designed with a greater affinity for CO_2 can improve its solubility on the membrane and can also be functionalized with reactive carriers to further increase the separation performance. Dispersion of inorganic particles in the polymer matrix to fabricate homogeneous membranes is one of the main challenges for MMMs. Voids between the inorganic filler and organic phase may reduce the overall selectivity (Dalane et al., 2017).

Membrane contactors are units where membranes act as a barrier between two phases. Mass transfer between these phases can be achieved without the dispersion of one phase into the other, combining the advantages of membrane separation and absorption processes. The selectivity of the separation is ruled by the selectivity of the solvent (either a physical or a chemical absorber). Although porous polymeric membranes are the most used contactors to minimize mass transfer resistance, inorganic membranes are also considered due to their stability. The main challenge of this technology is the decreased mass transfer due to the additional resistance of the membrane, especially when membrane pore wetting occurs. For gas-liquid membrane contactors with aqueous solvents hydrophobic membranes are favorable, as they avoid membrane wetting. The most studied polymers for membrane contactors are hydrophobic materials, such as polypropylene, polyvinylidene fluoride and polytetrafluoroethylene (Dalane et al., 2017).

Distillation

Further details of this process can be found in *4.6. Hydrocarbon recovery from syngas*.

Appendix 4. Description of methane recovery technologies

Adsorption

Adsorption of methane is mainly reported in activated carbons, MOFs and zeolites; with good selectivity CH_4/CO_2 in some cases (Alcañiz-Monge et al., 2009; Kim et al., 2013; Korman et al., 2020). This opens the door to the use of PTSA as a methane separation technology. Nevertheless, the technologies described are still at low TRLs and no methane-specific suitable technology has been found.

Absorption

The use of ionic liquids to absorb methane has been reported in the literature (Kim et al., 2013), but very few studies have been found. The technologies described are still at low TRLs.

Membranes

Studies has been found reporting the selective separation of CO_2/CH_4 mixtures (Kertik et al., 2017). The technologies described are still at low TRLs and no methane-specific suitable technology has been found.

Cryogenic distillation

Distillation of methane from a mixture of light hydrocarbons is detailed in *4.6. Hydrocarbon recovery from syngas*.

Appendix 5. Description of hydrocarbon recovery technologies

Cryogenic distillation

Cryogenic distillation is highlighted in the literature as a suitable technology for hydrocarbon and methane recovery from syngas.

This technology is based on the separation of a gaseous mixture by using simple distillation and operating at very low temperatures and high pressures. By doing so, dew points of the hydrocarbons are reached. Note that water and CO_2 melting points are above the operating temperatures of the column, so prior removal of these substances is required.

An application of cryogenic distillation for hydrocarbon and methane recovery from syngas is described in Al-Qahtani et al. (2017) and is adapted and explained below with the support of Figure A5.1.

1. The gas stream is fed to a heat exchanger that decreases its temperature, while condensing the heavier hydrocarbons of the mixture.
2. The stream enters a knockout drum that separates the condensed hydrocarbons from the rest of the gas.
3. Steps 1 and 2 are repeated until the feeding temperature of the column is achieved (around -150 °C). In each of this cooling steps, a hydrocarbon product comprising $C_2 – C_7$ in a liquid from is recovered. The system comprising all the heat exchangers and knockout drums used to decrease the temperature of the stream while recovering hydrocarbons is named “cold box system”.
4. The cooled gas is fed to a cryogenic separation unit, where syngas is separated from the C_1+ hydrocarbons.
5. The syngas stream is obtained at the top of the column and is used in the cold box system to decrease the temperature of the feed gas. It is finally recycled to the syngas conversion reactor.
6. The C_1+ stream is obtained at the bottom of the column and is fed to a demethanizer column together with the liquid hydrocarbon fractions obtained in the cold box system.
7. In the demethanizer, CH_4 is separated from the C_2+ hydrocarbons.
8. The methane stream is obtained at the top of the column. The distillate is linked to the cold box system together with an additional refrigeration cycle. It is finally recycled to the methane reformer reactor.
9. C_2+ stream is obtained at the bottom of the column.

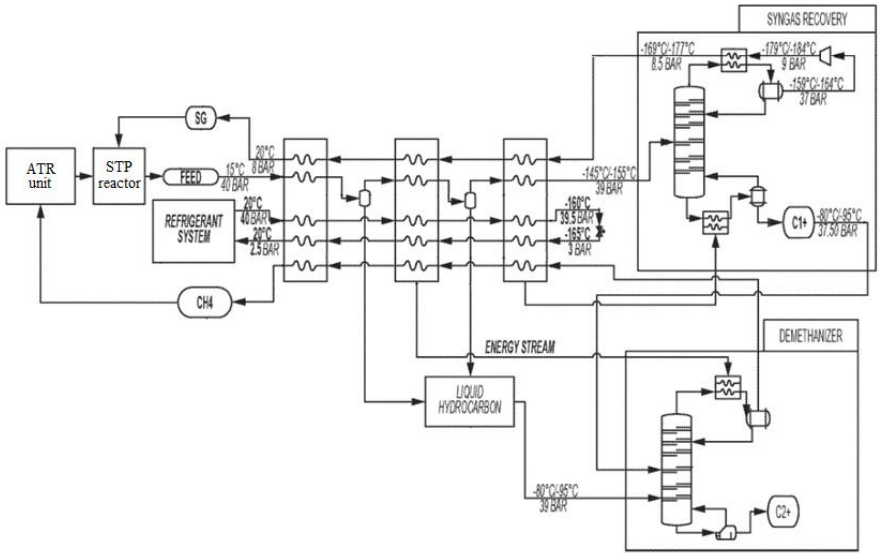

Figure A5.1. Cryogenic distillation scheme. Source: Al-Qahtani et al. (2017), modified.

Cryogenic distillation can provide a very high recovery of different components, but at a very high energy demand. Refrigeration duty is the main contributor, as very low temperatures must be achieved. To do so, refrigerants such as methane-nitrogen mixtures or individual ethylene and propane systems can be used. The capital cost of this technology is also high, as two distillation units are needed and refrigeration systems that achieve very low temperatures are required.

The energy demand of the system can be reduced by using JT expansion, turbo expansion or external refrigeration in combination with the demethanizer (Radique et al., 2015). Energetic integrations inside the system must be studied to further decrease the energy demand of the separation.

The elimination of the syngas recovery column can substantially decrease the energy demand of the system. By using a single column, methane and syngas would be recovered together, so methane could not be recycled to the methane reformer.

Recycle split vapor (RSV) is a technology developed by Ortloff Engineers, Ltd. for the recovery of hydrocarbons from natural gas streams. The configuration is similar to the previous technology after eliminating the syngas recovery column, but applying additional heat exchanges between the streams of the process and additional JT expansion and turbo expansion to the system. This way, the energetic requirements of the technology are reduced.

An application of the RSV technology is described by Campbell et al. (1995) and is explained below with the support of Figure A5.2.

1- The inlet gas is cooled in a system of heat exchangers (equivalent to the cold box system from Al-Qahtani et al., 2017).

2- The stream enters in a knockout drum where condensed hydrocarbons are separated from the rest of the gas.

3- The liquid stream is fed to the fractionation column.

4- The gas stream is divided in two streams.

5- The first gas stream is cooled in a heat exchanger and fed to the fractionation column.

6- The second gas stream enters a turboexpander to decrease its temperature. The stream is then fed to the fractionation column.

7- Natural gas is obtained at the top of the column and is used to refrigerate the first gas stream that enters the column and the cold box system.

8- The natural gas is compressed in the compressor of the turboexpander. The stream is further compressed.

9- Part of the natural gas is condensed with the distillate stream and fed in the fractionation column. This way, the reflux of the column has been stablished. Note that this may differ for syngas, as methane is easier to condense than CO.

10- Hydrocarbons are obtained at the bottom of the column.

Note that part of the cooling duty of the cold box system is provided by refluxes of the bottom of the column. Instead of a reboiler, heat is provided to the column by extracting energy from the cold box system.

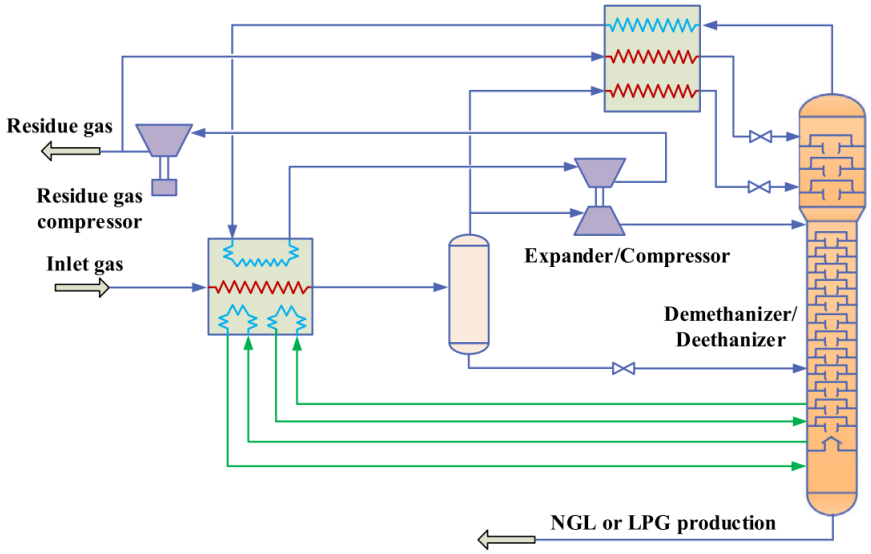

Figure A5.2. RSV process schematic. Source: Zhang et al. (2020a)

Similar systems have been developed for syngas by TechnipFMC or John Wood Group. Other configurations for natural gas found in the literature include “gas subcooled process”, “cold residue reflux”, “single-column overhead recycle”, “high-pressure absorber”, “recycle split vapor with propane refrigeration and pre-pressurization”, “recycle split vapor with propane and ethylene combined refrigeration” or “recycle split vapor with propane and mixed refrigerant refrigeration” (Hu et al., 2018; Zhang et al., 2020a).

Radique et al. (2015) warns that the energy efficiency of these hydrocarbon recovery systems from natural gas may not be extrapolated to hydrocarbon recovery from syngas due to the high content of hydrogen, that may decrease JT expansion cooling effect.

Extractive distillation

Rackley (2010) describes cryogenic distillation of light hydrocarbons from syngas in presence of CO_2 as a challenging operation for the following reasons:

1- Risk of solid carbon dioxide formation in the condenser due to the low temperatures at which the column must operate

2- Similarities in the vapor pressures of ethane and carbon dioxide at the operation temperatures

3- Formation of an azeotrope between CO_2 and ethane

Extractive distillation can overcome these challenges by the addition of a solvent which acts as an entrainer. The entrainer increases the temperature of the condenser, reduces the freezing temperature of carbon dioxide, breaks the azeotrope C_2H_6-CO_2 by increasing the relative volatility of these two compounds (Ebrahimzadeh et al., 2016).

Solvents recommended in the literature are lower molecular weight liquid oxygenated hydrocarbons such as alcohols, ethers or ketones; or C_3-C_8 hydrocarbons that can be obtained from cracking or other petroleum refinery operations (Patterson, 1952).

Some technologies focus on increasing the relative volatility of C_2H_6-CO_2 rather than breaking the azeotrope, promoting the separation of hydrocarbons from the rest of the gas at the cost of losing some ethane together with the carbon dioxide. An example is Ryan-Holmes' gas separation to obtain NGL, where C_5+ hydrocarbons already present in the feed are used as entrainers. The process is described by Rackley (2010) and is explained below with the support of Figure A5.3.

1. Gas is fed to a first distillation column together with the solvent. C_3+ and the entrainer are obtained at the bottom; and syngas, methane, carbon dioxide and ethane are obtained at the top.
2. The hydrocarbon stream obtained by bottoms is fed to an additive recovery column, where low molecular weight hydrocarbons are obtained at the top (main product) and heavier hydrocarbons are obtained at the bottom of the column (entrainer).
3. The entrainer stream is fed to the first column as the solvent, but also to the methane purification column (named as "methane removal" in Figure A5.3). Part of this stream is sent to the main product line to prevent solvent build-up.
4. The distillate from the first unit is compressed and fed to the carbon dioxide recovery column. Compression targets an increase of the temperature at the condenser to prevent CO_2 solidification and excessive energy consumption.

5. The bottom stream of the CO_2 recovery column is a mixture of carbon dioxide and ethane. Additional separation units such as amine wash, membranes or molecular sieves are still needed to remove carbon dioxide form the stream. Alternatively, the stream is sent to an enhanced oil recovery reservoir.
6. The distillate stream of the CO_2 recovery column (mainly methane and other entrained hydrocarbons) is fed to a methane purification unit (named as "methane removal" in Figure A5.3), where the C_5+ additive is injected to remove light hydrocarbons from methane. The stream obtained by bottoms is recycled.

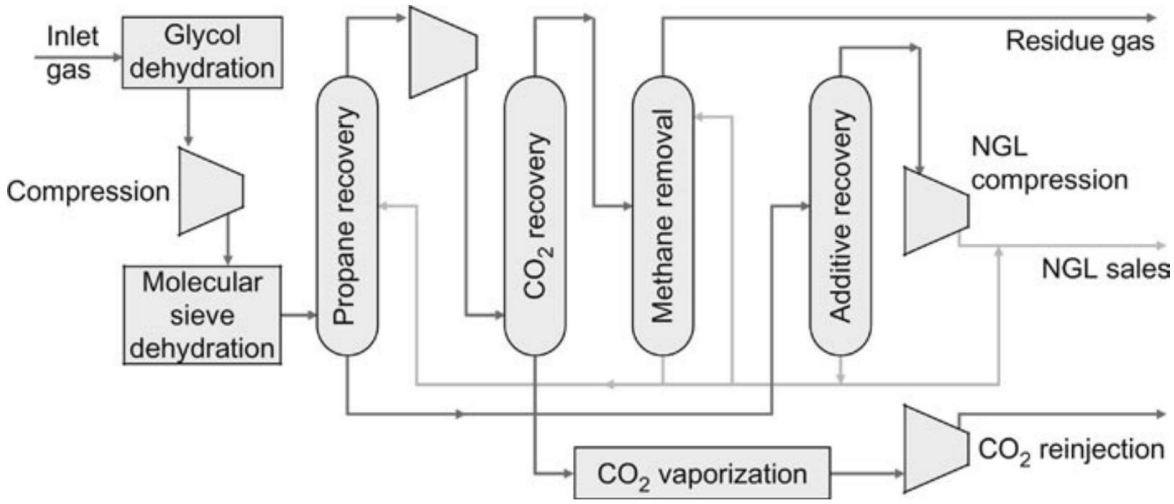

Figure A5.3. Ryan-Holmes separation process for the recovery of C3+ hydrocarbons. Source: Rackley, 2010.

As ethane is the main product of the syngas conversion process, C_2 must be recovered from the gas. This makes this technology non-suitable if no further CO_2 removal technologies are integrated in the process.

Other technologies such as classical extractive distillation focus on breaking the azeotrope. This process, using paraffines as entrainer, is described by Ebrahimzadeh et al. (2016) and is explained below with the support of Figure A5.4.

1. Gas is fed to a first distillation column together with the solvent (C_3+ hydrocarbons).
2. The entrainer breaks the azeotrope. Carbon dioxide and other lighter compounds are obtained as distillate; C_2+ hydrocarbons and the solvent are obtained by bottoms.
3. The hydrocarbon-rich stream is fed to a recovery column, where ethane (or other light hydrocarbons) is obtained as distillate and the solvent is obtained by bottoms and recycled to the first column as entrainer.

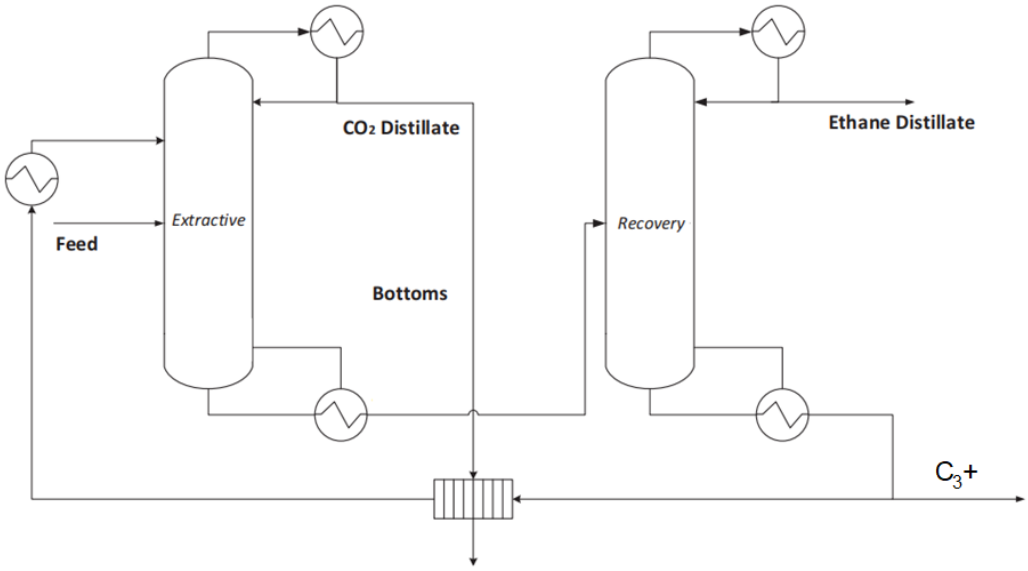

Figure A5.4. Conventional CO2-ethane separation with C3+ solvent. Source: Ebrahimzadeh et al. (2016), modified.

The configuration described is only valid for entrainers that modify the relative volatility of carbon dioxide and ethane so that $\alpha_{CO_2/C_2H_6} > 1$. For entrainers that invert their relative volatility, ethane is obtained as distillate of the first column and carbon dioxide is obtained by bottoms, changing therefore the configuration.

Extractive distillation can provide a very high recovery and a very good selectivity, but at a high energy demand due to the regeneration column operation and the refrigeration system needed. The use of two or more distillation columns is required together with a refrigeration system, so a high capital cost is also associated to this technology. Decreasing pressure can help by increasing the relative volatilities of the species of the mixture (potentially decreasing the amount of solvent used, translated into a lower energy demand), but it also decreases the boiling points of the substances of the mixture and, therefore, the refrigeration duty needed.

Authors in the literature describe different methods to reduce the energy demand of the system. For instance, suppressing the need of the recovery distillation column by the addition of a side rectifier (thermally coupled sequence) or by using a Petlyuk cryogenic extractive distillation column (Torres-Ortega et al., 2013) can reduce the energy consumption of the process. Ebrahimzadeh et al. (2016) study a measure diametrically opposed, as it is adding a third column to reduce the reflux ratios of the other two, leading to a decrease of recycle flow rates, entrainer use, heat duties and, overall, costs and energy demand. A common procedure for saving energy in industrial distillation columns is feed-splitting, that consists of heating whole or a portion of the feed with the column streams (Tavan et al., 2014a). The energy requirements of the system can also be reduced by using dividing-wall columns, which combines the operation of two conventional columns in one shell (Tavan et al., 2014b). In this application, the benefits of dividing wall columns are limited if the extractive distillation column and the regeneration column run at different pressures.

Pressure swing azeotropic distillation

This technology relies on the pressure sensitivity exhibited by azeotropes, enabling the separation of azeotropic mixtures without the need for entrainers. The process begins with the introduction of the feed stream into a high-pressure distillation column, where a conventional distillation operation is performed. The column yields one of the components of the azeotropic mixture at one end while obtaining the azeotropic composition at the opposite end. This last stream is directed to a second distillation column operating at a lower pressure. The decreased pressure induces a modification in the azeotropic composition, bypassing the azeotrope. At one end of this second column, the other component of the azeotropic mixture is obtained, while the stream at the other end with the modified azeotropic composition, is re-pressurized and recycled back to the first column.

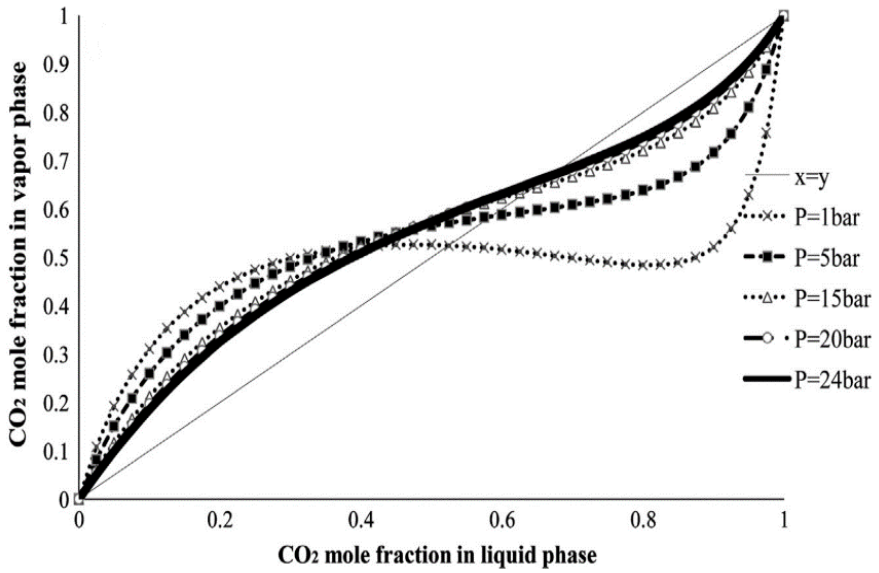

Figure A 5.5. x-y diagram of the mixture CO2-ethane.
Source: Tavan & Hosseini (2013), adapted.

Molecular sieves

Some authors describe this technology as suitable for syngas recovery from a mixture of methane and C_2+ hydrocarbons or for similar processes (Nyce et al., 2015; Radique et al., 2015).

The main characteristics of this technology have already been described in *4.2. Water removal*.

Different studies of gas-phase separations with MOFs have been reported in the literature, such as methane/carbon dioxide separation, or separation of light olefins and paraffins (Regufe et al., 2015). Vacuum pressure swing adsorption (VPSA) is a modification of the PSA technique that has also been reported in the literature to be useful for syngas processing by removing VOC (Chandran et al., 2018).

The use of this technology is only reported for methane and VOC, so the applicability is limited for these mixtures.

Fluidized sorption bed

Chandran et al. (2018) describes a continuous pressurized fluidized particulate bed as a suitable technology for VOC adsorption from syngas and is explained below with the support of Figure A 5.6.

1. The VOC-rich syngas is fed to the sorption bed. The gas is used to fluidize the particulate bed containing the adsorption medium.
2. Purified syngas leaves the reactor.
3. Solvent is directed to the regeneration heat exchange fluidized bed. Vapor is injected and heat is applied, desorbing VOC.
4. VOC laden regeneration vapors are extracted to be further processed.
5. Sorbent is recirculated to the main fluidized sorption bed

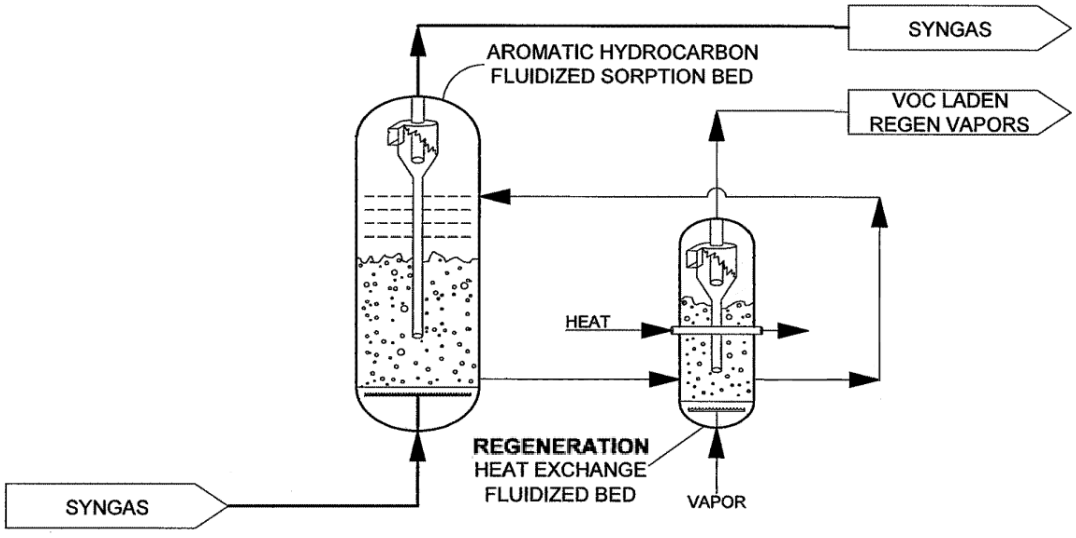

Figure A 5.6. Fluidized bed VOC adsorption system. Source: Chandran et al. (2018), modified.

Membrane separation technologies

Nyce et al. (2015) indicate membrane technologies as potential separation techniques for processes with streams of similar nature, such as for intermediate process streams from the oxidative coupling of methane or for the feed of the reactor from ethylene-to-liquids process.

Few literature sources have been found reporting membrane separation operations as a suitable technology for hydrocarbon recovery.

Appendix 6. Solvent screening for extractive distillation

Figures from A6.1 to A6.10 represent the variation of relative volatility using different solvents as entrainers. The objective is to demonstrate the potential of these solvents to be used in the extractive distillation. A good solvent must push the relative volatility away from 1 (azeotropic mixture) in low concentrations (low molar fractions).

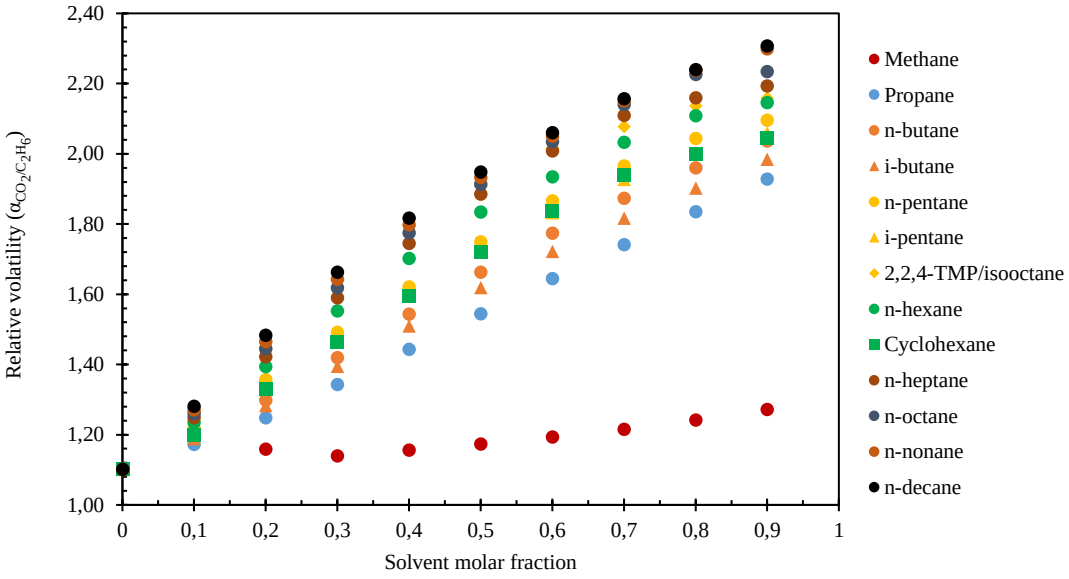

Figure A6.1. Relative volatility variation using alkane solvents as entrainer. Thermodynamic model used: PSRK.

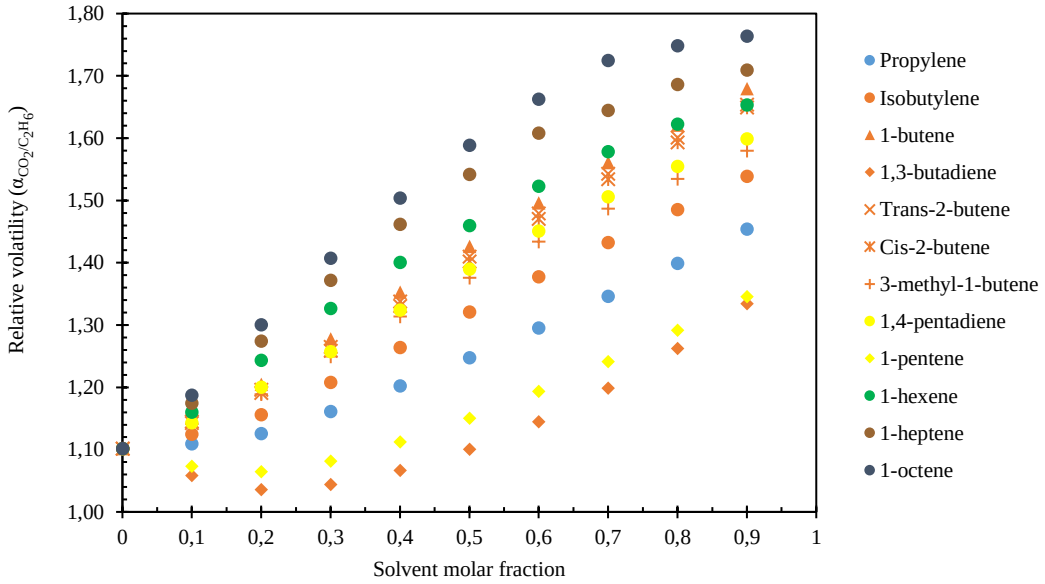

Figure A6.2.Relative volatility variation using alkene solvents as entrainer. Thermodynamic model used: PSRK.

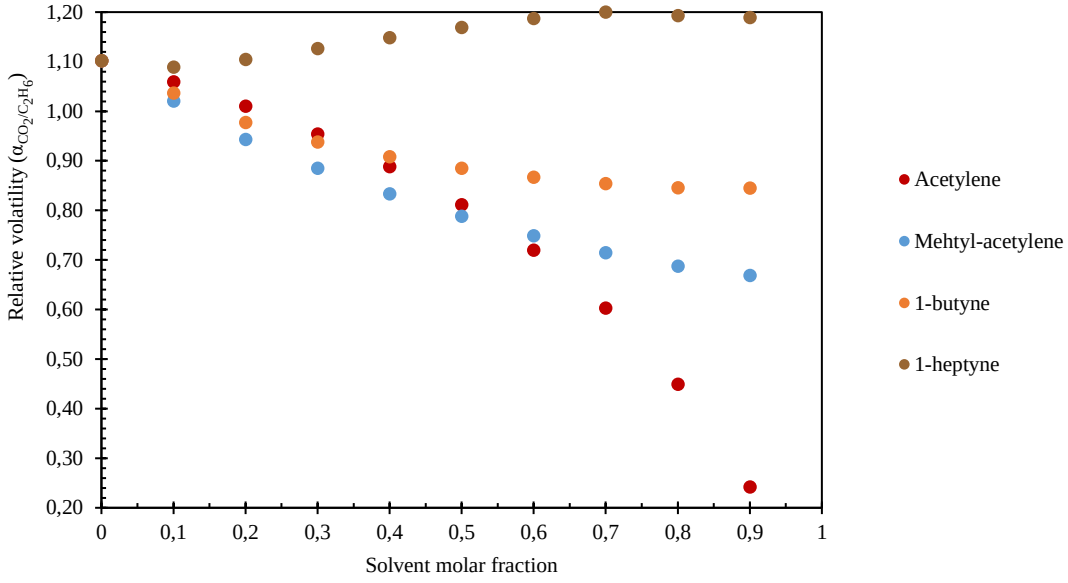

Figure A6.3. Relative volatility variation using alkyne solvents as entrainer. Thermodynamic model used: PSRK.

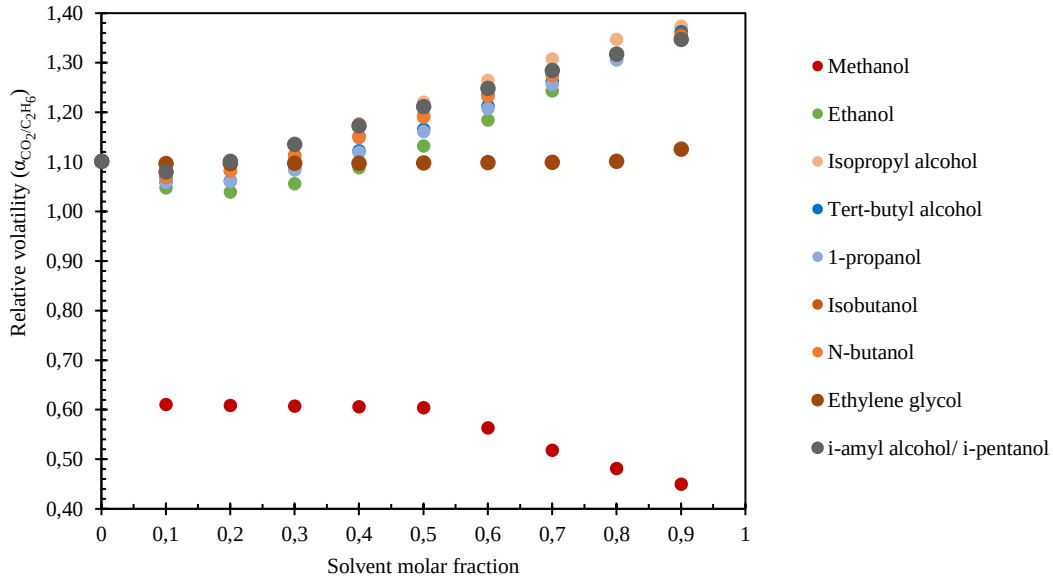

Figure A6.4. Relative volatility variation using alcohol solvents as entrainer. Thermodynamic model used: PSRK.

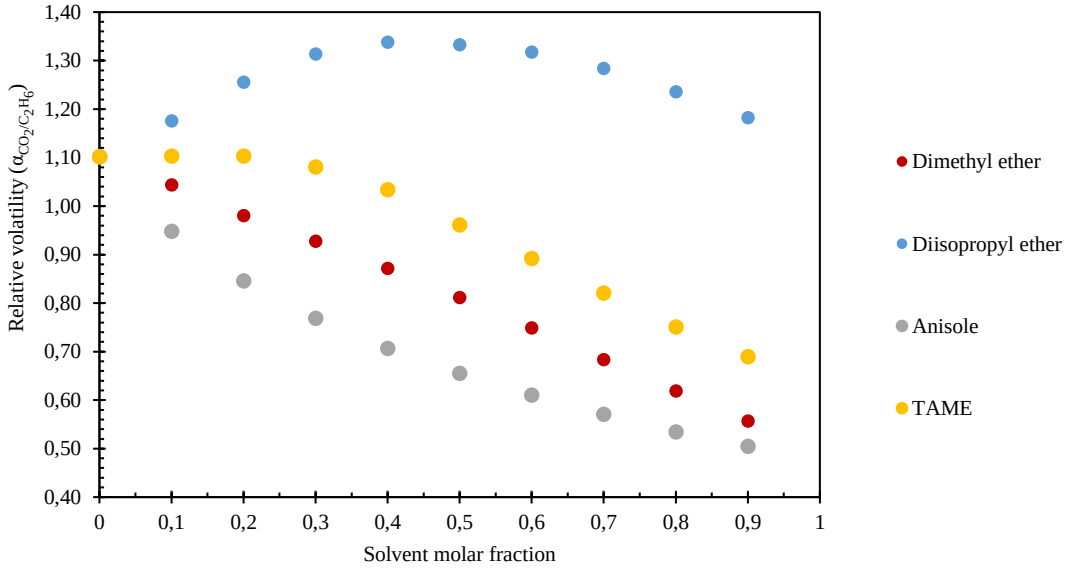

Figure A6.5. Relative volatility variation using ether solvents as entrainer. Thermodynamic model used: PSRK.

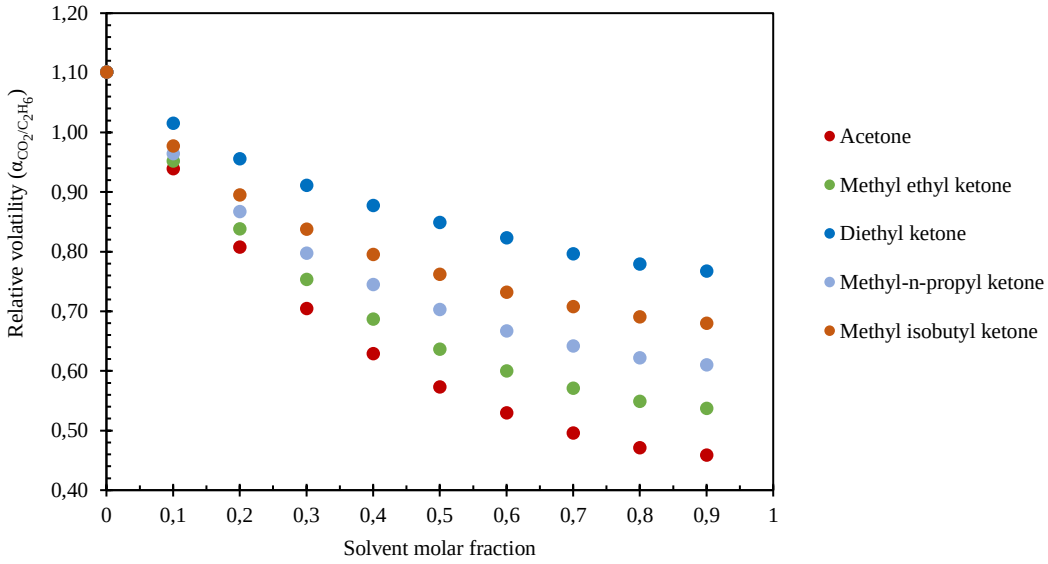

Figure A6.6. Relative volatility variation using ketone solvents as entrainer. Thermodynamic model used: PSRK.

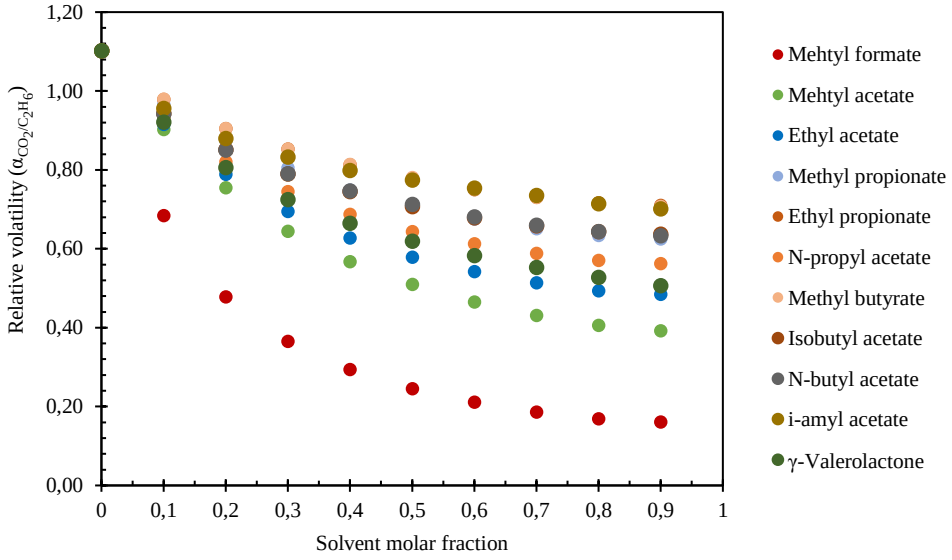

Figure A6.7. Relative volatility variation using ester solvents as entrainer. Thermodynamic model used: PSRK.

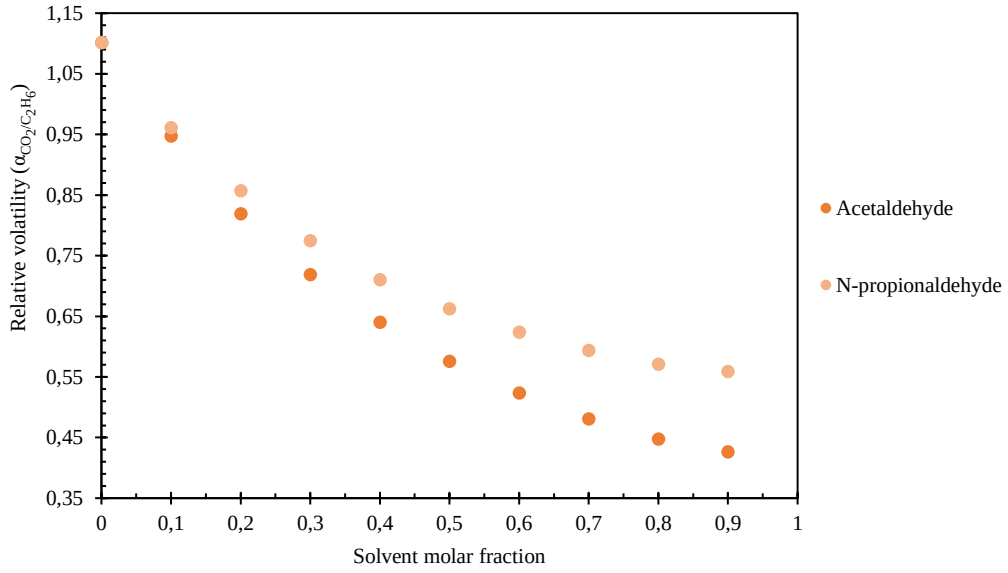

Figure A6.8. Relative volatility variation using aldehyde solvents as entrainer. Thermodynamic model used: PSRK.

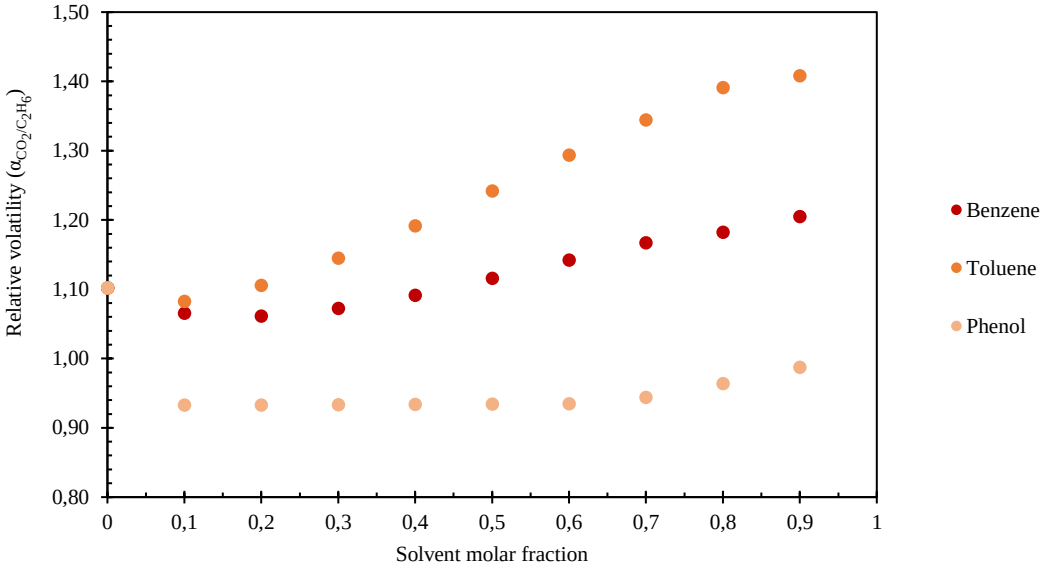

Figure A6.9. Relative volatility variation using aromatic solvents as entrainer. Thermodynamic model used: PSRK.

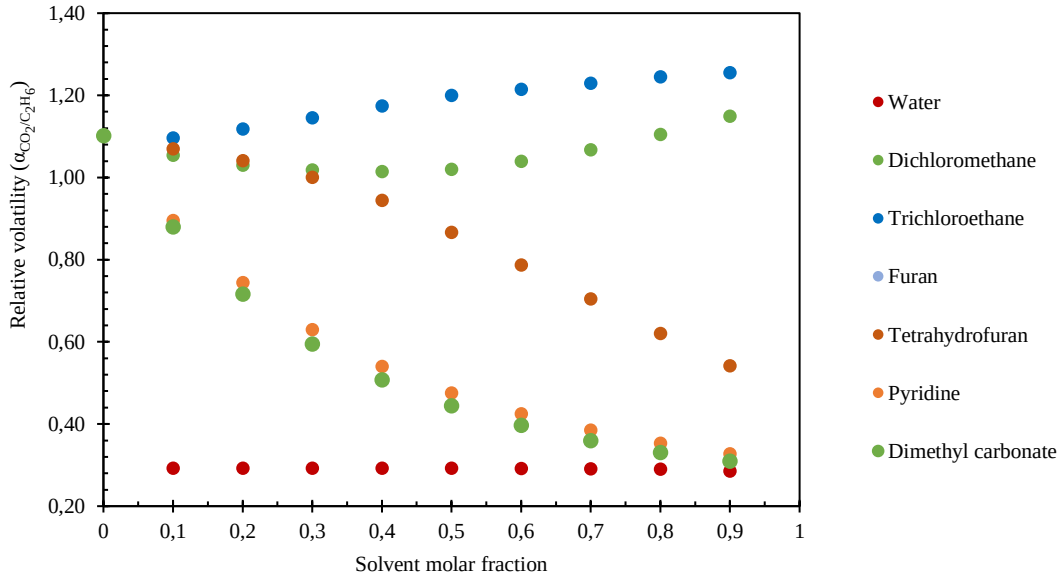

Figure A6.10. Relative volatility variation using alternative solvents as entrainer. Thermodynamic model used: PSRK.

Appendix 7. Energy consumption breakdown for water removal technologies

An energy consumption breakdown of Figure 6.1 (*6.1.1. Energy consumption analysis*) is found hereunder. Additional outcomes that are not mentioned in the main body of the project are listed at the end of the appendix.

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.1.1. Energy consumption analysis* are:

- Compression electrical power consumption for glycol absorption configurations using TSA as additional recovery is low. As glycol absorption is used as bulk removal, TSA is used in these cases as a rectifying unit, substantially decreasing the compression power dedicated to regenerate the catalyst.
- Cooling duty (condensation of water at 10 °C) is the main contributor of TSA power consumption. This highlights both the low energy consumption of molecular sieves, and the high consumption of refrigeration due to thermodynamic inefficiencies.
- Reboiler duty is the main contributor of glycol absorption power consumption, highlighting the high energy consumption of operation with solvents and the increased energy consumption associated to the operation of the system aiming very low concentrations of water in the dry gas.

Appendix 8. Sensitivity analysis of water removal capacity of TSA and glycol absorption

An energy consumption breakdown of Figure 6.2 (*6.1.2. Sensitivity analysis of the concentration of water in the dry gas*) is found hereunder. Additional outcomes not mentioned in the main body of the project are listed at the end of the appendix.

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.1.2. Sensitivity analysis of the concentration of water in the dry gas* are:

- Cooling power consumption is not affected by the water removal capacity of TSA. Pre-cooling the stream at 10 °C has been attributed to the water removal section of the process. As this pre-cooling is not part of TSA itself, and does not have an influence on the water removal capacity, its consumption is maintained constant at all concentrations of water studied.
- Heating and compression power consumption increase linearly when the water removal capacity of TSA increases (note that x-axis of *[deleted figure]* is not in linear scale). The lower the concentration of water aimed, the higher the mass of water adsorbed with the same operating time. As the mass of water to desorb is higher, the flowrate of regeneration gas must increase for the same operating times, increasing both compression and heating powers.
- Cooling, reboiler and pumping powers increase exponentially-like when the water removal capacity of glycol absorption increases (note that x-axis of *[deleted figure]* is not in linear scale) as a consequence of the behavior described by Henry's law. Compression power also increases exponentially-like under 20 ppmv. As the flowrate of solvent increases, the absorption of C_2+ in the solvent also does, increasing the compression power needed to re-compress the evaporated hydrocarbons during the de-pressurization of the solvent.

Appendix 9. Sensitivity analysis of the temperature of the gaseous feed for Rectisol®

An energy consumption breakdown of Figure 6.4 (6.2.1. Sensitivity analysis of the temperature in the absorption column for Rectisol® technology) and the results of the sensitivity analysis for the recovery of hydrocarbons are found hereunder. Additional outcomes not mentioned in the main body of the project are listed at the end of the appendix.

[Figures deleted for confidentiality purposes]

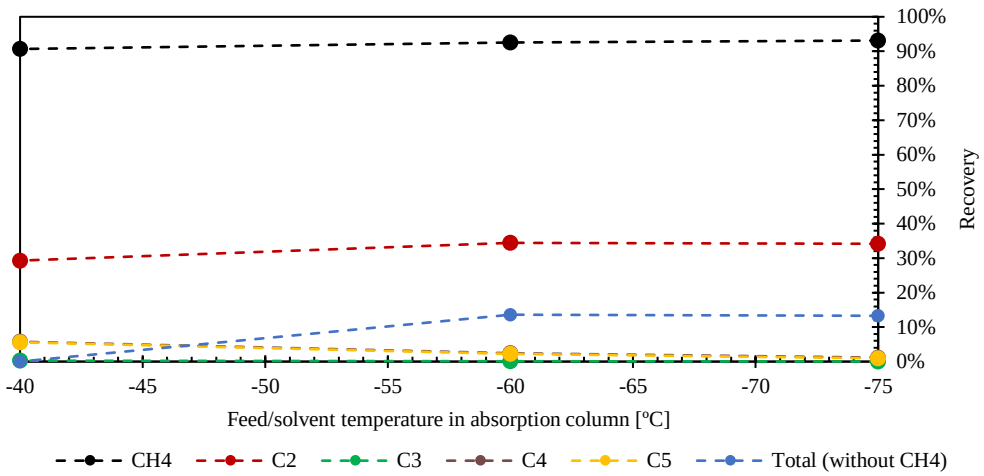

Figure A9.1. Hydrocarbon recovery for the sensitivity analysis of the temperature of the gaseous feed for Rectisol®.

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.2.1. Sensitivity analysis of the temperature in the absorption column for Rectisol® technology* are:

- Cooling thermal power consumption of each individual *HE-101(a-d)* is not affected by the feed temperature of the stream; but the overall *HE-101* increases when the temperature decreases. The individual requirement of each heat exchanger is not affected by the final feed temperature. However, when lower temperatures are aimed, additional heat exchangers are required, and the overall cooling power of *HE-101* increases.
- Condenser and reboiler thermal power consumption increase with temperature. When the temperature increases, the efficiency of absorption drops and the solvent flowrate required to achieve process specification increases. Higher solvent flowrates are translated in higher regeneration power consumptions (i.e., condenser and reboiler duties).
- Regeneration of the solvent represents 55 – 85 % of the total thermal power consumption and is the main unit contributing. This highlights the additional power consumption that implies operating with high flowrates of solvent.
- Compression power slightly increases with temperature. High temperatures promote the absorption of long-chain hydrocarbons, which end up in the CO_2-recovered stream and are re-compressed. This increases compression power consumption.
- Rectisol® solvent (methanol) has a high affinity for hydrocarbons regardless of the operation temperature, but has a higher affinity for long-chain hydrocarbons.

Appendix 10. Energy consumption breakdown for CO_2 recovery technologies

An energy consumption breakdown of Figure 6.5 (*6.2.2. Energy consumption analysis*) is found hereunder. Additional outcomes that are not mentioned in the main body of the project are listed at the end of the appendix.

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.2.2. Energy consumption analysis* are:

- Approximately 90 % of the cooling power consumption in Rectisol® is allocated in reducing the temperature of the feed to the operating temperature of the absorption column. Due to the heat integration of *HE-102* and *HE-103*, only 10 % of the cooling power consumption is allocated in reducing the temperature of the solvent after regeneration.
- Pumping electrical power consumption is slightly higher for amine wash. As most part of the solvent is only partially regenerated and acts as physical solvent (little chemisorption), the capacity of the total stream of amine to absorb CO_2 is reduced and the solvent flowrate is increased, enlarging the pumping electrical power consumption. Therefore, it becomes important to optimize the lean/semi-lean flow of amine solvent to reduce the overall energy consumption for a given CO_2 partial pressure driving force for absorption. Additionally, the amine solution is one order of magnitude more viscous than methanol, increasing the pumping electrical consumption.

Appendix 11. Sensitivity analysis of the CO_2 recovery capacity of Rectisol®

An energy consumption breakdown of Figure 6.6 (*6.2.3. Sensitivity analysis of the CO2 removal capacity*) is found hereunder. Additional outcomes not mentioned in the main body of the project are listed after the figure.

[Figure deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.2.3. Sensitivity analysis of the CO2 removal capacity* are:

- Cooling power consumption at -40 °C is not affected by the CO_2 removal capacity of Rectisol®. The power required to refrigerate the stream to the operating temperature of the absorption column is independent of the performance of the column.

- Cooling at -60 °C, pumping and reboiler power consumptions increase linearly down to 1000 ppmv; but the increment becomes exponentially-like for lower concentrations (note that x-axis of *[deleted figure]* is not in linear scale) as a consequence of the behavior described by Henry's law. Note that cooling power at -60 °C refers only to that of *HE-104* (Figure 5.5), as refrigeration duty to decrease the temperature of the feed to the operating temperature of the absorption column is not affected by the CO_2 removal capacity of the technology.
- Compression power consumption follows the same trend than cooling at -60 °C, reboiler or pumping power consumption. The exponential-like increase of solvent derives in an exponential-like increase of hydrocarbons that are absorbed in the absorption column. These end up in the distillate of the regeneration column and are compressed together with the carbon dioxide, leading to a substantial rise in compression energy.

Appendix 12. Energy consumption breakdown for cryogenic distillation

An energy consumption breakdown of Figure 6.8 (*6.3.1. Energy consumption analysis*) is found hereunder. Additional outcomes that are not mentioned in the main body of the project are listed at the end of the appendix. Table 6.3 of the main body of the project briefly describes each of the alternatives analyzed.

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.3.1. Energy consumption analysis* are:

- Reboiler duty thermal consumption is similar for all the configurations ([redacted] – [redacted] kW). Some cases worth mentioning are:
    - Alternatives 4, 8, 10 and 11 have slightly higher reboiler duties. This is caused by the modification of the operating conditions of the column. By increasing the operating pressure to increase the temperature profile of the column, relative volatilities are also modified. To achieve the same composition restrictions with the same (or similar) number of stages, the column needs to operate with higher reflux rates and increasing the reboiler duty.
    - Alternatives 5 and 7 also have slightly higher reboiler duties. In these cases, the feed is pre-cooled, increasing the reboiler duty in consequence.
- Cooling thermal power consumption for *HE-110* (source of refrigeration at -100 °C in the cold box) is similar for all the configurations ([redacted] – [redacted] kW) except for alternative *2.X*. By turbo-expanding the syngas recycle to obtain a temperature drop enough to allow heat transfer between the stream and the condenser of the column, additional heat can be extracted from the cold-box and the use of refrigerant at -100 °C is avoided.
- Pre-cooling of the column (*HE-122* in alternatives 5 and 7) is not effective to decrease the condenser thermal power consumption.
- Cooling thermal power consumption for *HE-112* (source of refrigeration at -130 °C in the cold box) is similar for all the configurations that use mixed refrigerant except for alternative *3.X*. As the reflux in the column is caused by transferring heat to the syngas recycle, the energy of the recycle is higher and cannot extract as much energy from the cold box system, increasing the consumption of *HE-112*.
- Compression electrical power consumption is higher for alternatives using turbo-expansion Some cases worth mentioning are:
    - Alternative *2.X* has the highest compressor power consumption among the alternatives using mixed refrigerant. As this configuration uses a pressure drop to further cool the syngas recycle, the decrease of pressure must be compensated by the compressor.

    - Alternative *9.X* has the highest compressor power consumption among the alternatives using turbo-expansion. This configuration uses the syngas recycle to create the reflux inside of the distillation column (acting as the condenser). By doing so, the energy of the stream is increased and the amount of energy that can absorb from *HE-112* is lower and the temperature reduction of the stream also is lower. When turbo-expanding the stream to achieve -150 ºC, the pressure drop needed is higher because the initial temperature has increased, and the consequent power to re-compress the stream is higher.

Appendix 13. Energy consumption breakdown of the comparison of cryogenic distillation for paraffins and olefins recovery

An energy consumption breakdown of Figure 6.11 (*6.3.4. Comparison of the primary separation unit for light olefins recovery*) is found hereunder. Additional outcomes that are not mentioned in the main body of the project are listed at the end of the appendix. **The following energy consumption analysis has been performed using a feed basis of 1000 kg/h.**

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.3.4. Comparison of the primary separation* unit for light olefins recovery are:

- For olefins recovery, cooling duties down to -100 °C are higher for the alternative using mixed-refrigerant; for paraffins recovery, both alternatives have similar cooling duties down to -100 °C. Condenser and reboiler duties have a similar behavior.
    - In olefins recovery, when turbo-expanding the stream, the pressure drop necessary to achieve -150 ºC is relatively high, reducing the total pressure to the half and modifying the vapor-liquid equilibrium of the mixture. As the pressure is lower, the flowrate of the syngas recycle stream is higher and the amount of energy that the stream can absorb is also higher, reducing the overall energy refrigeration demand of the cold box. In a similar way, as more flow has vaporized, the flowrate of the remaining liquid that is fed to the column is lower and the energetic consumption of the column is significantly lower too, as there is much less flow to process.
    - In paraffins recovery, the pressure drop when turbo-expanding the stream to achieve -150 ºC is relatively low, and the vapor-liquid equilibrium is not modified as dramatically as in the olefins recovery case. Similar recycles of syngas are obtained and a similar amount of energy from the cold box system is dissipated. The reason why the pressure drop is lower in paraffins recovery is that its feed is significantly richer in hydrogen than for olefins recovery.

Appendix 14. Energy consumption breakdown of the comparison of the results obtained for cryogenic distillation in the current project and in previous work

An energy consumption breakdown of

[Figure deleted for confidentiality purposes]

Figure 6.12 (*6.3.5 Comparison with previous work)* is found hereunder. **The following energy consumption analysis has been performed using a production basis of C_2 and C_3, instead of the production basis of C_2 used in the main body of the project.**

[Figures deleted for confidentiality purposes]

Appendix 15. Energy consumption breakdown for extractive distillation

An energy consumption breakdown of Figure 6.13 (*6.4.1. Energy consumption analysis*) is found hereunder. Additional outcomes that are not mentioned in the main body of the project are listed at the end of the appendix.

[Figures deleted for confidentiality purposes]

Some of the main outcomes that can be extracted from the models developed that are not already described in *6.4.1. Energy consumption analysis* are:

- Condenser thermal consumption for methanol extractive distillation columns have a higher energy consumption with a low C_2 recovery. As, in presence of methanol, ethane and ethylene are more volatile than CO_2, aiming low recoveries of C_2 at the top of the column is forcing the condensation of C_2, increasing the energy consumption.
- Amine wash reboiler duty consumption is negligible for extractive distillation using pentane, as most CO_2 has already been removed in the extraction column.

Appendix 16. Sensitivity analysis of the solvent flowrate for extractive distillation using pentane

An energy consumption breakdown of Figure 6.16 (*6.4.2. Analysis of the influence of flowrate of solvent*) is found hereunder.

[Figures deleted for confidentiality purposes]

Appendix 17. Sensitivity analysis of the temperature of the feed for extractive distillation using pentane

An energy consumption breakdown of Figure 6.18 (*6.4.3. Analysis of the influence of the temperature of the feed)* is found hereunder.

[Figures deleted for confidentiality purposes]

Appendix 18. Sensitivity analysis of the solvent purity after regeneration for extractive distillation using pentane

An energy consumption breakdown of Figure 6.19 (*6.4.4. Analysis of the influence of the purity of the regenerated solvent*) is found hereunder.

[Figures deleted for confidentiality purposes]

Appendix 19. Sensitivity analysis of the regenerated solvent recovery for extractive distillation using pentane

An energy consumption breakdown of Figure 6.20 (*6.4.5. Analysis of the influence of the recovery of solvent by bottoms in the regeneration column*) is found hereunder.

[Figures deleted for confidentiality purposes]

Appendix 20. Sensitivity analysis of the CO_2 recovery capacity for extractive distillation using pentane

An energy consumption breakdown of Figure 6.21 (*6.4.6. Analysis of the influence of the extraction column CO2 removal capacity*) is found hereunder.

[Figures deleted for confidentiality purposes]