Revaluation of the distillation column top purge streams

Master thesis presented by Maria Navas
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NOMENCLATURE

Acronym	Meaning
EU ETS	European Union Emissions Trading System
GHG	Greenhouse Gas
LYB	LyondellBasell
P&ID	Piping and Instrumentation Diagram
PE	Polyethylene
PFD	Process Flow Diagram
PP	Polypropylene
PPII	Polypropylene II
PPIII	Polypropylene III
SSE	Sum of Squared Errors
SST	Sum of Squares
MTC	Mass transfer coefficient

SUMMARY

This project addresses the treatment and valorisation of a gaseous residual stream generated during the extractive distillation of ethylene and propylene at LyondellBasell's [redacted] plant. This stream, withdrawn from the top of the distillation column, contains a mixture of ethylene, hydrogen, nitrogen, and trace amounts of propylene. The entrainment of these non-condensable components represents a loss of valuable product, mainly ethylene, and poses both energy and environmental challenges.

The initiative is aligned with the industry's interest in reducing emissions, maximizing resource utilization, and minimizing the environmental impact associated with the loss of light hydrocarbons. In this context, the objective of this work is to recover the ethylene present in the residual stream through a vacuum pressure swing adsorption (VPSA) process, an efficient gas separation technology based on selective adsorption onto a porous solid bed followed by vacuum desorption.

The first phase of the project consisted of characterizing the residual stream and selecting a suitable adsorbent. activated carbon was chosen due to its high adsorption capacity and selectivity for ethylene. Subsequently, the adsorption capacities of the main components (C_2H_4, N_2, and H_2) were determined by fitting experimental data to four thermodynamic models, selecting the one that best matched the experimental data for integration into the adsorption model.

Based on this data, a dynamic model of a multicomponent VPSA cycle was developed in Aspen Adsorption software, including the stages of adsorption, blowdown, rinse with high-pressure ethylene, and final desorption.

The process dynamics were evaluated through transient simulations and material balance analyses, allowing the assessment of system performance in terms of ethylene purity and recovery. The results demonstrate that the proposed VPSA system is technically feasible and enables the valorisation of a byproduct that would otherwise be discarded, yielding positive economic and environmental impacts. Additionally, key operating conditions were identified, laying the groundwork for the potential industrial implementation of the proposed system.

The final decision on adopting the process remains subject to the company's economic and strategic considerations; however, the findings of this study support a more efficient resource utilization and a move toward more sustainable operation.

Some parts of this work have been omitted or summarized due to confidentiality agreements with the collaborating company.

If you have any questions or would like more information (within what is permitted), please feel free to get in touch:

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Thank you for your understanding.

1. INTRODUCTION

In the current context of rising costs associated with CO_2 emissions in the European Union, the efficient management of residual streams has become strategically important. The stream addressed in this project, composed mainly of ethylene, hydrogen, and nitrogen, is generated as a byproduct in a distillation process aimed at separating ethylene and propylene. Its proper treatment through separation technologies, such as adsorption, enables not only the recovery and valorisation of the contained ethylene but also the minimization of the environmental and economic impacts linked to the European Union Emissions Trading System (EU ETS).

1.1. Contextualization: European regulatory framework and the need for CO2 reduction

The reduction of greenhouse gas (GHG) emissions, particularly carbon dioxide (CO_2), has become a strategic imperative for European industry, due to both environmental and economic implications. Within the framework of the European Green Deal, the European Union has committed to achieving climate neutrality by 2050, with an intermediate target of reducing net GHG emissions by at least 55% by 2030 compared to 1990 levels.[1]

One of the key instruments for achieving these objectives is the EU ETS. This system sets a cap on the total emissions of certain industrial facilities, which is progressively reduced each year. Companies must hold sufficient emission allowances (EUAs) to cover their annual CO_2 emissions, and those exceeding their allocated cap must purchase additional allowances on the market or face economic penalties.

The cost of emitting CO_2 has increased significantly in recent years. The price of emission allowances (per ton of CO_2 equivalent) has exceeded €80-100/tCO_2 in several periods since 2021, generating considerable economic pressure on energy, and emission, intensive sectors.[2] This situation has encouraged many industries to invest in emission mitigation technologies, including CO_2 capture and separation, to minimize their financial exposure.

In this context, the treatment and valorisation of residual gas streams have become strategically important. These streams, containing valuable components such as, in this case, ethylene, represent an opportunity to both optimize industrial process efficiency and reduce indirect CO_2 emissions associated with energy consumption and waste management. Among the available separation technologies, solid-phase adsorption stands out due to its high selectivity, low energy consumption, and operational flexibility, offering an effective solution for the recovery of valuable compounds from complex gas mixtures.

Thus, this project is conceived as a technical response aimed at optimizing a residual gas stream rich in ethylene, in order to recover valuable components and minimize associated environmental impacts. By recovering useful products and reducing energy losses, the project indirectly contributes to the reduction of CO_2 emissions and, consequently, to lowering the costs associated with the EU ETS compliance.

1.2. Propylene and polypropylene

Propylene is a key petrochemical intermediate, ranking second only to ethylene in global production volume. In 2022, worldwide propylene capacity was estimated at around 117 million tons, with continued growth projected at 5.54% through 2030.[3]

A major application of propylene is the production of polypropylene (PP), which consumes more than two-thirds of the total propylene output globally. For this purpose, polymer-grade propylene is required, typically with a purity higher than 99.5 wt.%. The increasing demand for polypropylene is fuelled by its favourable combination of properties such as high mechanical strength, chemical resistance, low density, and recyclability, positioning it as a viable substitute for polyethylene in many applications.

Advances in catalyst technology, especially Ziegler-Natta and metallocene catalysts, have expanded polypropylene's applications across industries such as packaging, automotive, and healthcare. Despite growing concerns over plastic waste, global demand for polypropylene remains strong, supported by its role in lightweight and durable products.

Leading global producers in the polypropylene market include ExxonMobil, Sinopec, LyondellBasell, and SABIC, which collectively dominate global production.[4]

1.3. Gas separation technologies

Before starting the in-depth study of the stream to be treated, different gas separation techniques that could be suitable for separating ethylene from the incondensable gases were explored.

1.3.1. Condensation

The method is based on lowering the temperature of a gas stream to a point at which the target component condenses, allowing its subsequent recovery in liquid form. This condensation can be achieved by increasing the pressure, decreasing the temperature, or applying a combination of both strategies; however, cooling is most commonly used due to its lower economic cost. Typically, this type of treatment is implemented as a pretreatment stage prior to other separation techniques, such as adsorption, among others.

In gas separation applications, this approach is mainly aimed at condensing ethylene to enable its reuse as a raw material. Its main advantages include operational simplicity and low implementation cost. However, it also presents notable drawbacks, such as low separation efficiency and a tendency for fouling in the equipment.[5]

Since the goal is to recover ethylene, the use of conventional cooling systems, such as water or propylene from the plant’s existing refrigeration unit, is not feasible, as they are unable to reach the sufficiently low temperatures required to liquefy ethylene, whose condensation temperature is significantly lower. The possibility of using liquefied ethylene from a new refrigeration system as a cooling medium was evaluated in order to condense the gas stream. However, the results showed that this solution only allowed the recovery of slightly less than 50% of the ethylene present in the mixture, and was therefore ultimately discarded. For more information, see Annex A.1.

1.3.2. Membrane

Membranes are thin structures that act as selective filters, allowing the preferential passage of certain gas components when specific operating conditions are met. Their ability to separate gases is based on the different interactions that each gas exhibits with the membrane material, resulting in varying permeation rates. These differences in transport across the membrane make it possible for some gases to diffuse faster than others, enabling effective separation.

Currently, there is a wide range of membrane technologies commercially available, including polymeric, ceramic, and hybrid variants. Although both the equipment design and system operation are relatively simple, this technique has some limitations, such as moderate separation efficiency and typically high investment costs.

Moreover, certain studies have shown that in mixtures containing ethylene, hydrogen, and nitrogen, reactions can occur on the membrane surface, leading to the formation of undesirable by-products such as ethane and methane[6]. For this reason, membranes are not considered the most suitable technology for the treatment of the stream under consideration. Consequently, their application is usually limited to systems where the gas flow rate is sufficiently high to justify the associated investment.[7]

1.3.3. Cryogenic distillation

Cryogenic separation is a technique commonly used in industry to recover and purify gases by taking advantage of their liquefaction at very low temperatures. This method is based on the differences in boiling points between the components of a gas mixture and typically requires intensive refrigeration systems, which operate through compression-expansion cycles along with the use of refrigerants such as liquid nitrogen.[8]

In this case, the presence of nitrogen and hydrogen hinders the selective condensation of ethylene, as it requires operating at extremely low temperatures and high pressures to prevent losses and unwanted carryover. Furthermore, the high energy consumption needed to reach cryogenic conditions makes this option less attractive from an economic standpoint.

1.3.4. Adsorption

Adsorption is a process by which gas molecules adhere to the surface of a porous solid. The attachment of the molecules to the solid surface can be driven by various factors, including differences in electric charge, possible chemical interactions, or compatibility in size and shape between the adsorbate and the adsorbent.[9]

Adsorbent materials have an extremely fine porous structure with spaces known as active sites. At these sites, the atoms of the solid have unsatisfied bonds, which allow them to attract and retain gas molecules that come into contact with them.

Depending on the type of interaction between the gas (adsorbate) and the solid (adsorbent), adsorption can be classified as physical, when the molecules are held by intermolecular forces such as Van der Waals interactions or hydrogen bonds, or as chemical adsorption, where the attractive force is comparable to a chemical bond.

This mechanism is widely used in gas separation and purification processes, especially when it is necessary to separate components present in very low concentrations or with similar physical properties, where other techniques may be less effective.

Adsorption systems operate cyclically and consist of at least two main steps: in the first, the gas comes into contact with the adsorbent, and the target compounds are retained; in the second, the adsorbent is regenerated by releasing the captured molecules, allowing the material to be reused in a new cycle. The method used for regeneration defines different technologies. If regeneration is achieved by lowering the pressure, the process is known as Pressure Swing Adsorption (PSA). If it is done by changing the temperature, it is called Temperature Swing Adsorption (TSA). There are also combined variants, such as Vacuum Pressure Swing Adsorption (VPSA), which applies vacuum during desorption to enhance performance.

This work proposes the use of VPSA technology to recover ethylene from a residual stream composed mainly of ethylene, nitrogen, and hydrogen, as it enables efficient separation without the need to apply extreme temperature or pressure conditions.

2. SCOPE OF THE PROJECT AND SPECIFIC OBJECTIVES

The objective of the project is to conduct a revaluation of the distillation column top purge streams from the polypropylene production plants PPII and PPIII. In addition, to evaluate the technical feasibility of implementing a VPSA system for the recovery of ethylene based on the results obtained.

- Perform a detailed characterization of the residual overhead stream generated in the ethylene/propylene distillation process, including operating conditions, composition, and the nature of the components present.
- Identify the most suitable separation technology for the recovery of the major component (ethylene), evaluating various available alternatives and selecting the process with the greatest technical feasibility for treating mixtures containing non-condensable gases.
- Gather and calculate all the necessary data for process simulation, including thermodynamic properties, adsorption equilibrium parameters, and representative operating conditions of the real system.
- Dynamically model the adsorption process using a multicomponent VPSA cycle with the Aspen Adsorption software tool, integrating the collected data to simulate the system's behaviour.
- Design the VPSA cycle's operational configuration, defining the required steps (adsorption, blowdown, rinse and desorption), and assess the influence of each step on product recovery and purity.
- Analyse the system's performance through simulations, determining the main operating variables that affect process efficiency and evaluating their sensitivity to changes in pressure, cycle times, and regeneration strategy.
- Estimate the preliminary environmental impact of the proposed system, assessing the emission reductions achieved by recovering ethylene compared to the current practice of flaring.

3. STUDENT'S ROLE IN COMPANY

3.1. LyondellBasell

LyondellBasell Industries N.V. is one of the world's largest chemical companies, specialising in the production of plastics, chemicals and fuels. It is incorporated in the Netherlands and has its operational headquarters in Houston, Texas, with additional offices in Rotterdam and London. As of 2021, LYB reported revenues of approximately $46.2 billion, with a workforce of around 19,300 employees worldwide.

LyondellBasell was formed in December 2007 through the acquisition of Lyondell Chemical Company by Basell Polyolefins in a transaction valued at approximately $12.7 billion. Basell was a leading polyolefins producer, the result of a merger of several European companies and owned by entrepreneur Leonard Blavatnik's Access Industries.

LyondellBasell with a purpose of *Creating solutions for everyday sustainable living*, is a world leader in the production of polyolefins, including polyethylene (PE) and polypropylene (PP), and in the development and licensing of associated processing technologies. Its products are used in a wide range of applications, from packaging and automotive components to medical supplies and textiles. The company also produces commodity chemicals such as ethylene and propylene, as well as fuels and fuel additives. In addition, it offers patented technologies. Therefore, the various fields in which the company is present are:

- Chemicals: Production of essential chemical compounds, such as ethylene, propylene, butadiene, methanol and vinyl acetate. These products are used as raw materials in multiple industries, including adhesives, paints, textiles and plastics.
- Polymers: The company is a world leader in the production of polyethylene (PE) and polypropylene (PP), materials used in the manufacture of packaging, films, consumer goods and automotive parts.
- Advanced Polymers: specialising in advanced polymers, offering high-performance solutions for demanding applications in sectors such as automotive, electronics, construction and technical packaging. This line includes reinforced polypropylene compounds, technical resins, thermoplastic elastomers and special blends.
- Fuels: operation in the energy sector through the production of fuels and additives such as reformulated gasoline and methyl tert-butyl ether. Although it has reduced its direct presence in this segment, it still represents a strategic component of its historical portfolio.
- Technology: The company is a leading provider of technology licenses for the production of polyolefins such as Spheripol, Hostalen and Lupotech. These technologies are used by petrochemical companies globally in the construction and operation of new production plants.

LYB operates in more than 100 countries, as it can be seen in Figure 3.1, and has production facilities in North America, Europe, Asia and Australia. In Europe, it has a significant presence in countries such as Germany, France, Italy and Spain.

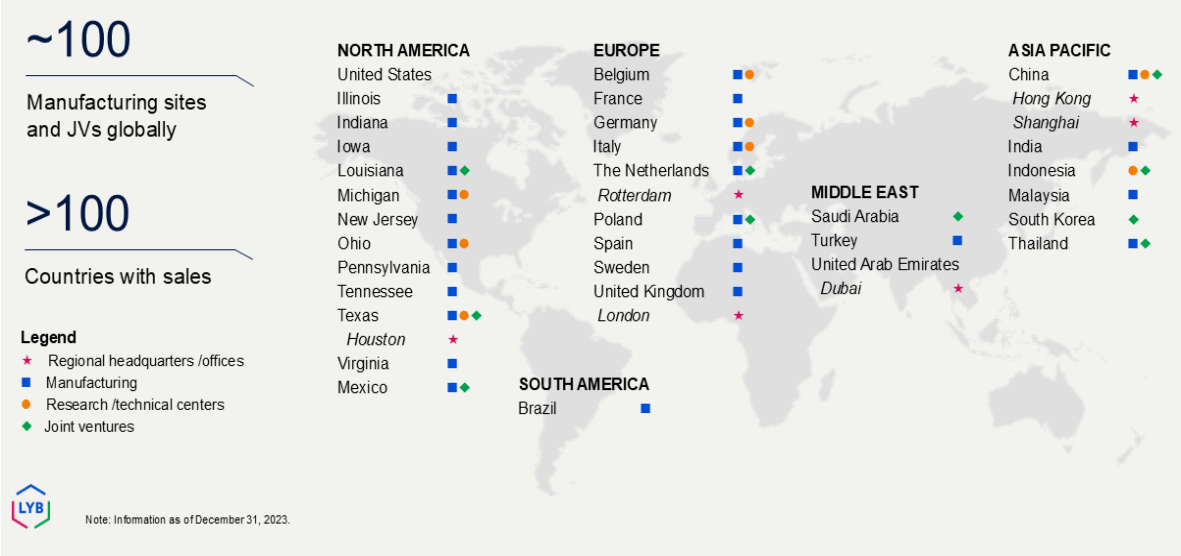


Figure 3.1. LyondellBasell presence around the world.

The company maintains a significant presence in Spain, with operations spread across several locations. The headquarters are in Barcelona, while production plants are located in Castellón and Tarragona. The latter is divided into two distinct areas: the eastern area houses the polypropylene production plant, known as PP, and is mainly dedicated to the manufacture of this polymer. On the other hand, the western area in Tarragona, called PPC, houses the corporate offices along with an extrusion plant that operates nine lines. These lines specialise in the compounding process of polypropylene, which allows its properties to be modified according to the specific needs of its final application.

Figure 3.2. Site location of LYB in Tarragona.

LYB has taken initiatives to promote the circular economy and reduce its carbon footprint. Its *Circulen* product line includes recycled and renewable-based polymers, contributing to its customers' sustainability goals. In addition, LyondellBasell participates in programmes to improve workplace safety and health, such as its *GoalZERO* initiative, which aims for zero incidents in its operations.

So, LYB has a company mission to be the preferred partner of its customers by providing sustainable and circular solutions through innovation , operational excellence and value

creation, with a vision to lead towards a more sustainable future, with an emphasis on driving a circular economy, being a leader in sustainability, providing innovative solutions and creating value for all stakeholders, guided by the following values:

- Commitment to people: Placing people at the centre of all actions, promoting a diverse, equitable and inclusive culture.
- Pursuit of excellence: Constantly raising standards through collaboration and a passion for global impact.
- Shaping the future: Making environmentally conscious decisions, fostering creative solutions and a pioneering mindset.

4. THEORETICAL BACKGROUND

4.1. Adsorption fundamentals

To understand the basic principles of adsorption, it is useful to differentiate between physical and chemical adsorption. In physical adsorption, the forces that hold the molecules to the surface of the material are weak, such as Van der Waals forces. In chemical adsorption, on the other hand, stronger bonds, similar to those that occur in a chemical reaction, are generated between the adsorbed compound and the surface of the adsorbent. The characteristics that distinguish these two types of adsorption are summarised in the table below.

Table 4.1. Differences between physical and chemical adsorption.[9]

Physical Adsorption	Chemical Adsorption
Low enthalpy of adsorption	High enthalpy of adsorption
Not highly specific	Highly specific interaction with the surface
Can form single or multiple layers	Limited to monolayer
No dissociation occurs	Adsorbed species may undergo dissociation
Relevant at low temperatures	Slow at low temperatures, fast at high temperatures
Fast process, generally reversible with no activation energy required	Requires activation energy and may be irreversible
Without electron transfer	Electron transfer due to chemical bond formation

Most gas separation processes based on adsorption, such as the one proposed in this work, rely on physical adsorption. This is because chemical adsorption, being limited to a single molecular layer, generally results in lower loading capacities, which can reduce its economic viability in industrial applications.

The role of the adsorbent is to provide a large surface area for the selective attachment of the target molecules. Therefore, it is important for the adsorbent to have both good selectivity and a sufficiently high adsorption capacity, since this directly affects the size and cost of the adsorption beds. For this reason, commercial adsorbents are typically made from microporous materials.

The heat of adsorption provides an estimate of the strength of the interaction between the adsorbate and the surface.

From a thermodynamic point of view, physical adsorption is an exothermic process, which means that heat is released during the interaction between the gas molecules and the surface of the solid. This is reflected by a negative change in enthalpy (H <0). Additionally, the process involves a decrease in entropy (S <0), since the gas molecules transition from a free and disordered state to a more ordered one as they become confined on the surface of the adsorbent. The spontaneity of the process is assessed through the change in Gibbs free energy (G), which is calculated using the following relation:

$$\Delta G = \Delta H - T\Delta S \tag{4.1}$$

Since both H and S are negative, the enthalpy of adsorption must be sufficiently large for the change in Gibbs free energy to also be negative ΔG <0). This typically occurs at low temperatures, where the term $-T\Delta S$ does not dominate the equation. As previously mentioned, this behaviour demonstrates that the adsorption process enhances the stability of the system by

reducing its total energy. Therefore, the heat of adsorption can be considered proportional to the strength of the interaction between the gas and the surface of the solid.[9]

4.2. Adsorption equilibrium

To describe the equilibrium established between the adsorbent and the adsorbate, a series of mathematical models are used. Adsorption on solid surface typically occurs at constant pressure. Therefore, the phenomenon is commonly analysed and modelled using adsorption isotherms.

Equilibrium is established when the adsorbent and the adsorbate remain in contact for a sufficient period of time, during which the adsorbate concentration changes, allowing the analysis of the adsorption kinetics. After this period, the adsorbate concentration becomes stable, indicating that equilibrium has been reached.

4.2.1. Henry's law

Molecules that are attached to the surface of a solid can be considered as an additional phase from a thermodynamic point of view, different from the surrounding gas phase. The behaviour of this phase is determined by the principles of thermodynamics, which establish the equilibrium between the adsorbed species and its environment.

As explained above, physical adsorption is exothermic. This characteristic makes the process more efficient at low temperatures, while at higher temperatures desorption, i.e. the detachment of the molecules from the solid, is favoured.

When working with low adsorbate concentrations, the equilibrium between the amount adsorbed and the adsorbate pressure can be approximated linearly. This relationship is known as Henry's Law and can be expressed as follows:

$$q = KP \tag{4.2}$$

Where q is the adsorbed concentration, P is the partial pressure of the gas, and K is Henry's constant. This constant is the adsorption equilibrium constant, and its temperature dependence follows the Van't Hoff relation:

$$K = K_o e^{-\Delta H/RT} \tag{4.3}$$

Following Equation 4.1, in an exothermic process, ΔH and ΔS are negative, therefore, Henry's constant decreases with increasing temperature.

4.2.2. BDDT classification of isotherms

The great majority of isotherms can be classified into five different types according to the Brunauer-Deming-Deming-Teller (BDDT) classification of isotherms.[10]

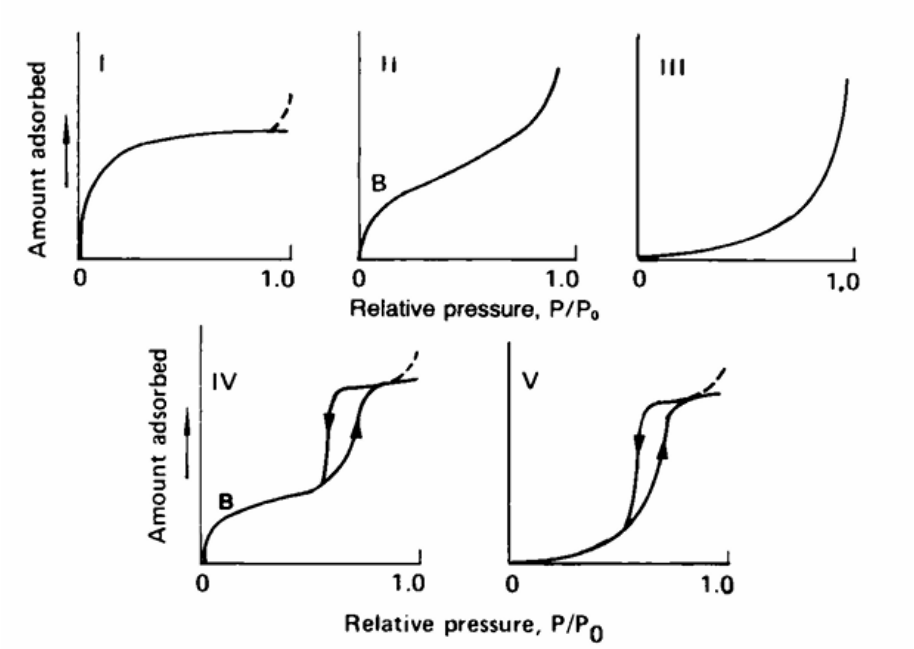


Figure 4.1. Types of adsorption isotherms according to the BDDT classification.

Type I is characteristic of monolayer adsorption on microporous surfaces, such as activated carbon and certain molecular sieves. Type II corresponds to adsorption on a non-porous surface, with an inflection that marks the filling point of the monolayer towards multilayer formation. Type III occurs when the adsorbate-adsorbent interactions are weak, its convex shape indicates a progressive adsorption without apparent saturation. Type IV and V curves correspond to adsorption on mesoporous materials. Type IV indicates good initial affinity and shows capillary condensation with hysteresis, typical of mesoporous silicas. Type V, on the other hand, reflects low initial affinity between adsorbate and adsorbent, with capillary condensation at high pressures and also exhibits hysteresis, but with a lower adsorption capacity.

Hysteresis is the difference between the adsorption and desorption curves, due to effects such as capillary condensation, and is indicative of the porous structure of the material.

Type I and type II isotherms are the most common in PSA systems.

4.2.3. Equilibrium models

Before selecting the most appropriate isotherm to describe the equilibrium of the process, a theoretical framework of the different equations studied is presented.

4.2.3.1. Langmuir isotherm

The Langmuir model describes adsorption as a dynamic phenomenon mainly associated with chemical adsorption processes, and provides a sound theoretical basis for interpreting the behaviour of isotherms. This model assumes that all active sites available on the adsorbent surface are uniform and equivalent, and that each of them can be occupied by a single molecule, implying monolayer adsorption. Furthermore, it is assumed that there is no interaction between the already adsorbed molecules. This type of isotherm is compatible with Type I isotherm in de BDDT classification.

When equilibrium is reached, the adsorption rate of the molecules on the surface becomes equal to the desorption rate, resulting in a steady state.

The general adsorption reaction, assuming that there are a fixed number of sites present on the adsorbent surface, can be represented as follows:

$$A + S \leftrightarrow AS \tag{4.4}$$

Where A is the molecule in the gas phase, S is the free site on the surface of the solid and AS represents a free site occupied by A.

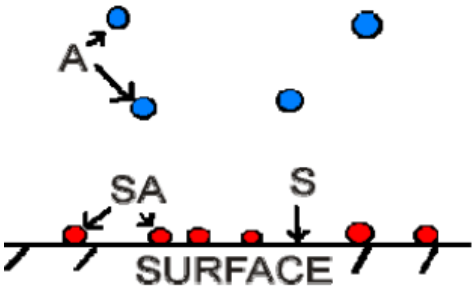


Figure 4.2. Schematic representation of the adsorption mechanism on a solid surface.[11]

At equilibrium, the adsorption rate equals the desorption rate.

$$K_a[A][S] = K_d[AS] \tag{4.5}$$

Where $K_a[A][S]$ is the rate of the adsorption reaction (r_{ads}) and $K_d[A][S]$ is the desorption rate (r_{des}). Parameter $[A]$ represents the equilibrium concentration of the species A in the gas phase and $[AS]$, $[S]$ are the concentration of occupied and free adsorbent surface spaces, respectively.

Langmuir expressed the fraction of occupied sites on the surface as θ $(0 < \theta < 1)$, and considered $[AS]$ to be proportional to the surface coverage of the adsorbed molecules, that is, proportional to θ. Therefore, $[S]$, or in this case $1 - \theta$, represents the fraction of available sites on the solid. $[A]$ is proportional to the number of collisions, meaning it is related to the gas pressure. Consequently, the adsorption rate is proportional to the partial pressure and to the remaining vacant surface of the adsorbent.

$$r_{ads} = K_a P_i (1 - \theta) \tag{4.6}$$

The desorption rate is proportional to the fraction of the adsorbent surface that is occupied.

$$r_{des} = K_d \theta \tag{4.7}$$

Using the principle of equilibrium in adsorption, the adsorption rate is equal to the desorption rate.

$$r_{ads} = r_{des} \tag{4.8}$$

As a result, the following equation is obtained:

$$K_a P_i (1 - \theta) = K_d \theta \tag{4.9}$$

Defining θ as the ratio between the amount adsorbed on the surface of the solid, qi, and the maximum adsorption capacity, q_{max}, equation 8 can be expressed as:

$$K_a P_i \left[\frac{q_{max}-q_i}{q_{max}}\right] = K_d \left[\frac{q_i}{q_{max}}\right] \quad (4.10)$$

$$K_a P_i (q_{max} - q_i) = K_d \quad q_i \quad (4.11)$$

If the ratio between K_a and K_d is defined as K_L,, the Langmuir model takes the following form:

$$q_i = q_{max} \frac{K_L P_i}{1+K_L P_i} \quad (4.12)$$

This equation allows the adsorption behaviour to be modelled over a wide range of pressures. At low pressures, the model predicts a linear relationship between q_i and P_i,, while at high pressures an asymptotic saturation toward q_{max} is observed, reflecting the complete filling of the available adsorption sites.

4.2.3.2. Freundlich isotherm

The Freundlich isotherm was one of the first models used to describe adsorption processes involving the formation of multiple layers. According to this model, the amount of adsorbed material depends on the properties of the adsorbent, the concentration of the adsorbate, and the temperature. It assumes that the surface of the solid is not uniform and that there are differences in adsorption energy across various sites, as well as possible interactions between adsorbed molecules. This kind of isotherm is compatible with Type II isotherm in de BDDT classification.

This model is frequently used to represent gas adsorption on heterogeneous surfaces at constant temperature. The Freundlich equation indicates that as the available sites on the solid become occupied, the energy with which new molecules adhere gradually decreases.

Unlike the Langmuir model, the Freundlich isotherm does not define a maximum adsorption capacity. This makes it more suitable for describing processes that occur under low to moderate pressure conditions. The model also suggests that the sites with the highest energy are occupied first, resulting in stronger binding of the initial molecules. As these high-energy sites become saturated, the remaining molecules adsorb onto lower-energy areas, forming weaker bonds. In other words, the adsorption energy decreases as the amount of adsorbate retained on the surface increases.

The exponential isotherm is presented as follows:

$$q_i = K_F P_i^{1/n} \quad (4.13)$$

Where K_F is the adsorption capacity constant and n is the heterogeneity parameter, both constants for the same temperature. n reflects how the affinity of the adsorption sites changes as the surface coverage increases.

- n =1: indicates a homogeneous surface with equivalent adsorption sites, resulting in linear adsorption.

- n >1: suggests a heterogeneous surface where high energy sites are saturated first, and adsorption occurs at lower energy sites as the surface coverage increases.
- n <1: implies cooperative adsorption, although this situation is less common in real systems.

4.2.3.3. Langmuir-Freundlich isotherm

The Langmuir-Freundlich isotherm, also known as the Sips isotherm, is a model that combines elements from both of the original isotherms to represent the distribution of adsorption energy on adsorbent surfaces with heterogeneous characteristics. This isotherm is particularly useful when the adsorbent has sites with varying energy levels, meaning the surface is not uniform. This isotherm is generally associated with Type I isotherm in de BDDT classification.

The general equation of the Langmuir-Freundlich isotherm is expressed as:

$$q_i = q_{max}\left(\frac{K_{LF}\,P_i^n}{1+K_{LF}\,P_i^n}\right) \tag{4.14}$$

Where q_{max} is the máximum capacity of adsorption, K_{LF} is the model constant, and n the heterogeneity parameter.

When the exponent n is equal to 1, the Langmuir-Freundlich isotherm reduces to the classical Langmuir isotherm, implying a homogeneous system of equivalent adsorption sites. However, for values of n less than 1, the model reflects the typical behaviour of a heterogeneous surface, similar to that described by the Freundlich isotherm.

4.2.3.4. Toth isotherm

The Toth isotherm is a modified version of the Langmuir equation. This model introduces an additional parameter that allows the heterogeneity to be adjusted over wide pressure ranges. The following relation describes the Toth isotherm:

$$q_i = q_{max}\frac{K_T\,P_i}{[1+(K_T\,P_i)^n]^{1/n}} \tag{4.15}$$

Similar to the Langmuir-Freundlich isotherm, when the parameter n =1, the equation reduces to the Langmuir form, representing a homogeneous surface. For values of n <1, the model reflects a decrease in adsorption energy as the surface coverage increases, as is the case for heterogeneous surface adsorbents.

4.3. Adsorption kinetics

During the adsorption process of gases, mass transport from the gas phase to the solid surface can be limited by various resistances. They are mainly classified into the resistance to mass transport from the gas phase to the gas-solid interface, and the resistance associated with diffusion within the porous structure of the adsorbent.

One way to represent these resistances in a simplified way is by means of a global resistance model that unifies both effects into a single kinetic parameter. This approach is known as the Lumped Resistance Model and allows the time evolution of the adsorbed quantity to be described by means of a linear kinetic expression.[12]

$$\frac{dq_i}{dt} = MTC_i(q_i^* - q_i) \tag{4.16}$$

Where $q_i$is the adsorbed amount of component i on the solid, q_i^* is the equilibrium charge corresponding to the gas phase at that instant, MTC_i is the mass transfer coefficient of component i, and t is the time.

4.4. Adsorption dynamics

The reliability of an adsorption process does not depend solely on equilibrium, although equilibrium isotherms provide information on the maximum adsorption capacity of the adsorbent at given conditions, they do not take into account mass transfer limitations, the physical structure of the adsorbent or the influence of operating parameters such as pressure, temperature or flow rate.

To evaluate the performance of an adsorbent under realistic conditions, one of the most commonly used tools is the breakthrough curve. This curve is obtained by performing a dynamic adsorption experiment in a fixed-bed column, where the feed gas flows through a packed bed of adsorbent. By monitoring the concentration of the target component, in this case ethylene, it is possible to determine how long it takes for the adsorbent to become saturated. A typical breakthrough curve is shown in Figure 4.3.

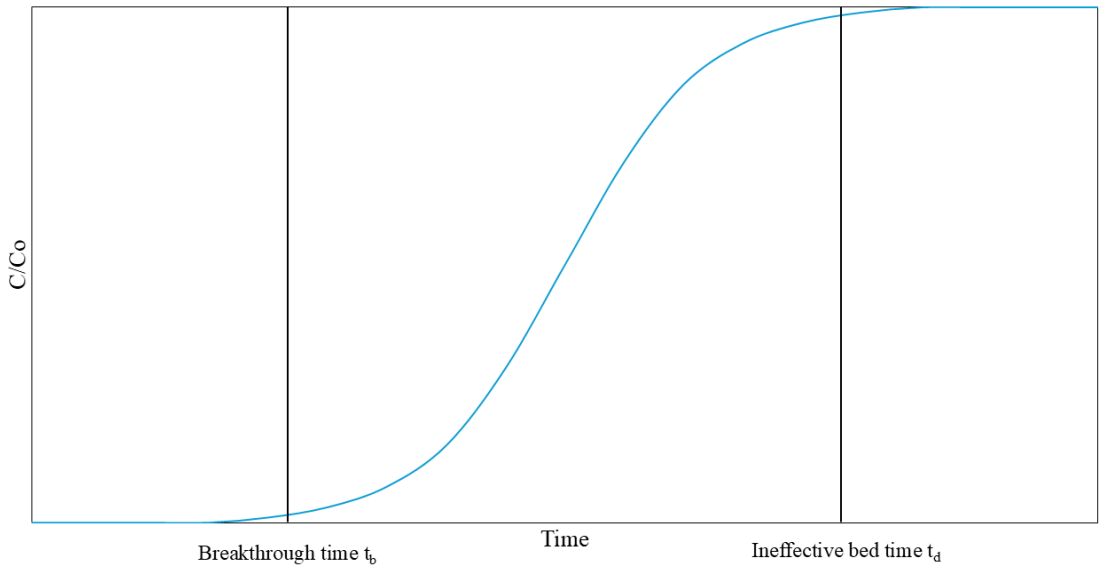


Figure 4.3. Typical breakthrough curve.

Two key time points are commonly used to describe the breakthrough curve:

- Breakthrough time, tb in Figure 4.3: usually defined as the time when the component's output concentration is approximately 5% of its input concentration. It is a practical indicator of when the adsorbent starts to lose its effectiveness.
- Ineffective bed time, td in Figure 4.3: this is the time when the component output concentration approaches 95% of the feed composition. At this point the bed is considered fully saturated.

Between the two points is the mass transfer zone, MTZ, where the adsorption front advances along the bed. The length and shape of the MTZ provides information on the kinetics and transport phenomena within the column. A narrow, sloping MTZ indicates favourable kinetics with minimal dispersion, whereas a wider MTZ is a sign of internal or external diffusion limitations.[13]

4.5. Bed regeneration process

As mentioned above, once the adsorbent is saturated, it must be regenerated. This is usually achieved by modifying the thermodynamic operating conditions, such as temperature or pressure. The variants that give the regeneration process its name are Pressure Swing Adsorption (PSA), Temperature Swing Adsorption (TSA) and Vacuum Pressure Swing Adsorption (VPSA).

4.5.1. Pressure Swing Adsorption (PSA)

In a PSA system, the regeneration of the adsorbent takes place through a cycle that combines a pressurisation and a depressurisation phase. During the high pressure stage, the gas molecules are retained on the surface of the adsorbent material due to the increased affinity between the two. As the pressure is reduced, this interaction decreases, making it easier for the gas to be released from the solid, leading to regeneration.

Although PSA systems can be more efficient than TSA processes, they tend to be more energy intensive, especially due to repetitive compression and decompression operations.[14]

4.5.2. Temperature Swing Adsorption (TSA)

Regeneration in a TSA process is based on increasing the bed temperature to reduce the affinity between the adsorbent and the adsorbate. As the physical adsorption is an exothermic process, the temperature increase favours the desorption of the retained gas. During this stage, a hot gas stream is introduced or direct heat is applied to the bed, releasing the adsorbate which is then evacuated. The system must cool down before a new cycle.

Although TSA allows effective regeneration, its main disadvantage is the high energy consumption and long cycle times due to the heating and cooling of the bed.

4.5.3. Vacuum Pressure Swing Adsorption (VPSA)

The working principle of a VPSA combines pressure adsorption with vacuum regeneration. In processes where adsorption occurs at elevated pressures, the adsorbent loading capacity improves, but the energy cost increases significantly due to the compression work and the use of vacuum pumps for desorption.

Unlike a conventional PSA, where no vacuum is needed to desorb, VPSA can achieve higher recovery or purity, but at the cost of higher overall energy consumption.

5. METHODOLOGY

In this section, the techniques and methods used to achieve the proposed objectives and to obtain results are described.

In order to study the composition of the streams to be treated and their subsequent treatment by adsorption, the following approach was established:

1. Preliminary study of separation methods: as reflected in the introduction to the project, a preliminary study was carried out of the methods available for the treatment of the gaseous current, with the final choice of technology to be studied.

2. Product selection: Due to the diverse palette of products available and their different recipes, it is important to identify those that provide the most value in terms of the content of the compounds under study and the production plan of the company.

3. Analysis and calculation of the composition of the vent-gas stream: Process data from the DCS of both plants and from PFDs were collected as they are essential inputs for the subsequent analysis of the stream composition using material balance principles.

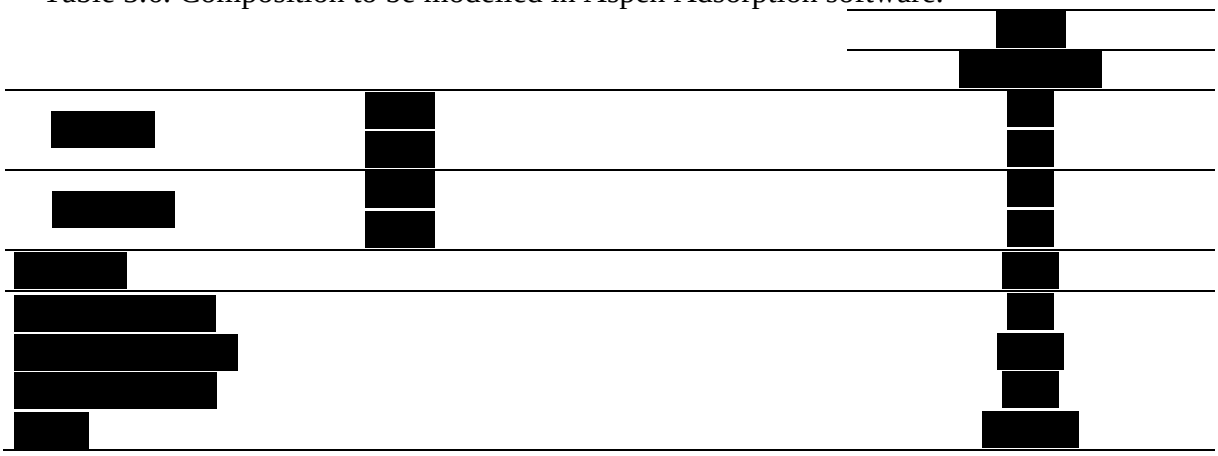
4. Selection of the adsorption isotherm and comparison of adsorbents: Study and comparison of different adsorption equilibrium models, based on experimental data for the compounds of interest, applied to two adsorbents. The most suitable models and materials are selected accordingly.

5. Programming in Aspen Adsorption software: simulation, design and dynamic modelling of the adsorption process using Aspen Adsorption software, based on previously estimated composition data and operating conditions taken from the real process. Special focus placed on the behaviour of ethylene as preferent adsorbable component.

5.1.1. Selection of the vent-gas composition to be modelled

Based on the analysis of the available compositions in both plants, several limitations were identified that make it difficult to select a common representative stream. Firstly, each plant operates with an independent production schedule, which means that the products manufactured at each site differ in both timing and composition. This complicates the definition of a single, stable composition that could represent the entire system.

Table 5.6. Composition to be modelled in Aspen Adsorption software.



5.2. Aspen Adsorption software programming

When starting the simulation in Aspen Adsorption software, the first step is to define the involved species and the calculation method to be used.

In this simulation, the definition of the components and the calculation of thermodynamic properties were previously carried out in Aspen Plus, using the Peng-Robinson equation of state, as stated earlier in this work, to describe the non-ideal behaviour of the gas mixture composed of ethylene, hydrogen, and nitrogen.

Subsequently, the properties calculated in Aspen Plus are transferred to Aspen Adsorption software through the automatically generated property file. This file contains the necessary information about the mixture, including enthalpies, activity coefficients, heat capacities, viscosities, and other physical properties.

However, it is important to note that, within the Aspen Adsorption software model, the gas flowing through the bed is defined as an ideal gas, and therefore follows the ideal gas law.

$$PV = nRT \tag{5.6}$$

Where P is the pressure, V the volume, n the number of moles, R the gas constant, and T the temperature. This model assumes that there are no molecular interactions between species and that the molecular volume is negligible, which significantly simplifies thermodynamic calculations.

This assumption is justified in preliminary design stages or when operating under moderate pressure and temperature conditions, where the compressibility factor Z of the gaseous components approaches 1.

Table 5.6. presents the mass composition of the main components of the stream, C_2H_4, N_2, and H_2, obtained from the procedure previously described. However, since Aspen Adsorption software uses molar flow by default as the calculation basis for streams, it was necessary to convert the mass fraction to mole fraction in order to adapt the data to the format required by the simulator.

This conversion was carried out using the molar masses of each component, according to the following expression:

$$y_i = \frac{\left(\frac{w_i}{M_i}\right)}{\Sigma_j\left(\frac{w_j}{M_j}\right)} \tag{5.7}$$

Where y_i is the mole fraction of component i, w_i is the mass fraction and M_i is the molar mass of component i.

The molar compositions of the three components are shown in Table 5.29.

Table 5.29. Mass and mole compositions of the inlet gas.

[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]

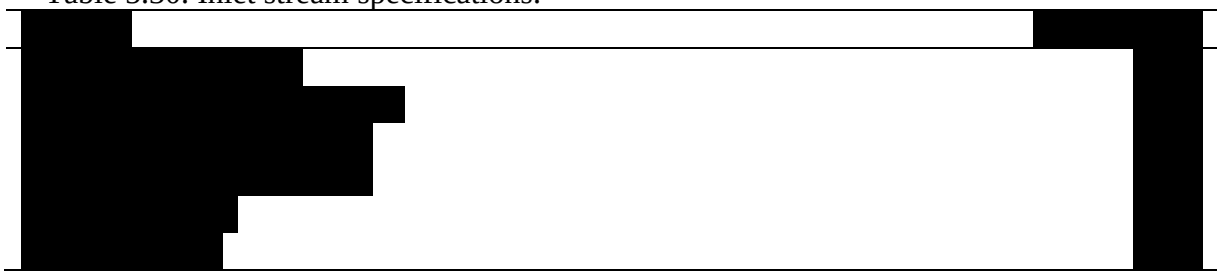
Once the physicochemical properties of the system have been configured using Aspen Plus, it is necessary to design and define the model that the bed will follow. For this purpose, a simpler simulation is performed, including only the adsorption step, without incorporating the other elements that will be present in the complete simulation cycle.

This simulation includes the feed stream, an outlet stream through which the components not retained by the adsorbent are expelled from the bed, and the adsorption bed itself, as shown in Figure 5.19.

Figure 5.19. Initial scheme for model definition.

The first element to be defined in the simulation is the inlet stream, as shown in the following table.

Table 5.30. Inlet stream specifications.



To convert the mass flow rate to molar flow rate, the following relation was used:

$$\dot{n} = \frac{\dot{m} \cdot 1000}{MW_{prom} \cdot 3600} \tag{5.6}$$

$$MW_{prom} = \sum_i y_i MW_i \tag{5.7}$$

Where $\dot{n}$ is the total molar flow rate (mol/s), $\dot{m}$ is the total mass flow rate (kg/h), MW_{prom} is the average molecular weight of the mixture (g/mol), y_i is the mole fraction of the component

i, MW_i is the molecular weight of component, 1000 is the conversion factor from kilograms to grams, and 3600 is the conversion from hours to seconds.

[redacted] It is worth noting that in Aspen Adsorption software within the feed gas stream configuration module, there is an interdependence between pressure and flow rate: when one of these parameters is fixed, the other becomes a degree of freedom. In this case, the inlet pressure of the feed stream has been fixed. Subsequently, by adjusting the pressure drops in the different steps of the cycle through the advanced simulation settings, the resulting flow rate is brought close to the specified design flow rate.

When defining the outlet stream, it is once again necessary to consider the degrees of freedom of the model. Therefore, pressure and temperature must be specified for this stream, while the remaining variables are left unspecified and change over time, as shown in Table 5.31.

Table 5.31. Outlet stream specifications.

[redacted]

In the case of the bed, where the equations governing the system are configured, it is necessary to define the discretization, the mass and momentum balances, the kinetic model, the type of isotherm model, and the energy balance.

The bed used in this work consists solely of a single adsorbent, activated carbon, arranged in a vertical position. Since the mobile phase is gaseous, gravitational effects on the flow can be neglected, promoting a uniform axial distribution of the gas. The spatial dimension is 1-D, meaning that variable changes are considered only along the height of the bed, while a uniform distribution is assumed in the radial and angular directions.

5.2.1. Discretization

To solve the differential equations that govern the behaviour of the adsorption bed, Aspen Adsorption software uses the USD1 (Upwind Differencing Scheme 1) discretization scheme. This method, based on a first-order Taylor series expansion, enables a stable and efficient numerical formulation, particularly suitable for solving hyperbolic equations in transient regimes, as is the case in pressure swing adsorption processes.

The upwind scheme is characterized by using information from the upstream node of the flow to calculate the convective transport terms, which reduces the risk of numerical instability. The general formulation of this method for the first spatial derivative is as follows:

$$\frac{\partial \Gamma_i}{\partial z} \approx \frac{\Gamma_i - \Gamma_{i-1}}{\Delta z} \tag{5.8}$$

Whereas for the second spatial derivative, required in certain diffusive terms, the following expression is applied:

$$\frac{\partial^2 \Gamma_i}{\partial z^2} \approx \frac{\Gamma_{i+1} - 2\Gamma_i + \Gamma_{i-1}}{\Delta z^2} \tag{5.9}$$

The bed domain is discretized into a series of finite nodes. The number of nodes must be defined in the software prior to the simulation, as it determines the spatial accuracy of the model. A higher number of nodes results in greater fidelity in the resolution of concentration and pressure profiles, although at the expense of increased computational time. In this case, the number of modules is predefined by Aspen Adsorption software as 20 modules.[12]

5.2.2. Mass and momentum balance

In this work, a one-dimensional (1-D) convective flow model under transient conditions has been considered, without axial dispersion. For this assumption, the *Convection Only* option is selected, eliminating the dispersion term from the mass balance. As a result, the model represents plug flow with a dispersion coefficient of zero.

The gas-phase mass balance for component i is expressed as:

$$\frac{\partial (v_g c_i)}{\partial z} + \varepsilon_i \frac{\partial c_i}{\partial t} + \rho_s \frac{\partial q_i}{\partial t} = 0 \tag{5.10}$$

Where v_g is the interstitial gas velocity (m/s), c_i is the concentration of component i in the gas phase (mol/m3), ε_i is the interparticle voidage (-), ρ_s is the adsorbent density (kg/m3), q_i is the adsorbed loading of component i (mol/g), z is the axial coordinate along the bed and t is the time.

Regarding the momentum balance, to specify how the adsorption bed model handles gas velocity and pressure, the Ergun equation has been used. This equation combines the description of pressure drops through the Karman-Kozeny equation for laminar flow and the Burke-Plummer equation for turbulent flow, making it the most commonly used option for solving this type of model.[12]

$$\frac{\partial P}{\partial z} = -\left(\frac{1.5E{-}03(1-\varepsilon_i)^2}{(2 r_p \psi)^2 {\varepsilon_i}^3} \mu v_g + 1.75E-05\, M \rho_g \frac{(1-\varepsilon_i)}{2 r_p \psi {\varepsilon_i}^3} {v_g}^2 \right) \tag{5.11}$$

Where ε_i is the interparticle voidage of component i, ψ is the shape factor and r_p is the particle radius.

5.2.3. Kinetic model

As presented in Section 4.3, the assumed kinetic model is the Lumped Resistance Model in its linear form (Equation 4.16), expressing the mass transfer driving force as a function of the adsorbed loading on the solid. The mass transfer coefficient (MTC) is assumed to be constant for each adsorbates.

Table 5.32. Mass transfer coefficients.[17]

[redacted]

5.2.4. Isotherm

To implement the Langmuir-Freundlich isotherm in Aspen Adsorption software, its extended multicomponent version has been selected. This formulation allows for modelling competitive adsorption among the different components of the mixture, under the assumption that all species compete for the same active sites, but with different affinities and capacities.

The general expression for the multicomponent Langmuir-Freundlich isotherm is:

$$q_i = q_{i,max}\left(\frac{K_{i,LF}\,P_i^{n_i}}{1+\sum_{j=1}^{N} K_{j,LF}\,P_j^{n_j}}\right) \tag{5.12}$$

However, in Aspen Adsorption software, it is expressed as:

$$q_i = \frac{IP_{1i}IP_{2i}P_i^{IP3_i}e^{IP4_i/Ts}}{1+\sum_j\left(IP_{5j}P_k^{IP3_j}e^{IP6_j/Ts}\right)} \tag{5.13}$$

By comparing both equations, it can be observed that:

- $IP1 = q_{max}\ (mol/g)$
- $IP2 = IP5 = K_o\ (1/bar)$
- $IP3 = n\ (-)$
- $IP4 = IP6 = \frac{-\Delta H}{R}\ (K)$

The IP coefficients to be provided to Aspen are the following:

Table 5.33. Langmuir-Freundlich isotherm coefficients to be entered into Aspen Adsorption software.

[redacted]

5.2.5. Energy balance

Finally, the energy balance assumption is defined. In this work, an isothermal simulation has been considered, meaning there is no heat exchange and the temperature of the gas and the solid remains the same. As mentioned earlier, the temperature used in the simulation is [redacted]

The specific design of the heat exchanger, as well as its integration with the rest of the plant, is not addressed in this work, as it is considered outside the scope of the project. However, it is assumed that such a device will be present in the actual installation to ensure that the stream enters the PSA system at the operating temperature considered in the simulation.

5.2.6. Bed specification

Once the bed model has been defined, it is necessary to introduce the characteristic parameters of the bed and the adsorbent in order to solve all the equations. The considered values for these parameters in the simulation are included in Table 5.34.

Table 5.34. Characteristic parameters of the bed and activated carbon.[15]

[redacted]

The dimensions of the bed have been determined in such a way as to minimize the pressure drop within the adsorption column, while ensuring sufficient residence time for the adsorption of the target components to occur. In particular, a balance has been sought between the bed length, which influences separation efficiency, and the diameter, which directly affects the pressure drop according to the Ergun equation.

5.3. Aspen Adsorption software simulation

Once the equations governing the behaviour of the bed have been defined and the basic adsorption process has been initiated, additional key elements are incorporated into the process diagram, such as valves, dead volume tanks, and the various gas inlet and outlet streams.

The system configuration follows the structure shown in the following figure.

Figure 5.20. Process diagram simulated in Aspen Adsorption software.

Before defining the specifications of all the elements included in the simulation, the steps that make up the operating cycle of the simulation are explained:

1. Feed (FD): The vent-gas stream with the selected composition is fed into the column, during which ethylene is selectively adsorbed while nitrogen and hydrogen exit through the top of the column via the off-gas stream. Before the ethylene concentration begins to rise in the off-gas stream, the feed is shut off.

Figure 5.21. Representation of valve states during the feed step.

2. Depressurization (DP): After the feed step, the feed valve is closed whereas the off-gas valve remains open, and the pressure in the column is reduced to , thereby displacing part of the feed gas volume retained inside the column.

Figure 5.22. Representation of valve states during the depressurization step.

3. Rinse (RN): When the column reaches 6 bar a, the rinse stream is opened. Following a widely practice in CO_2 capture systems[18], where the target compound is used as the purge gas, ethylene is employed in the rinse stream. By introducing ethylene into the column, the residual feed gas retained inside the bed is displaced and replaced with ethylene, significantly increasing the purity of the ethylene recovered during desorption.

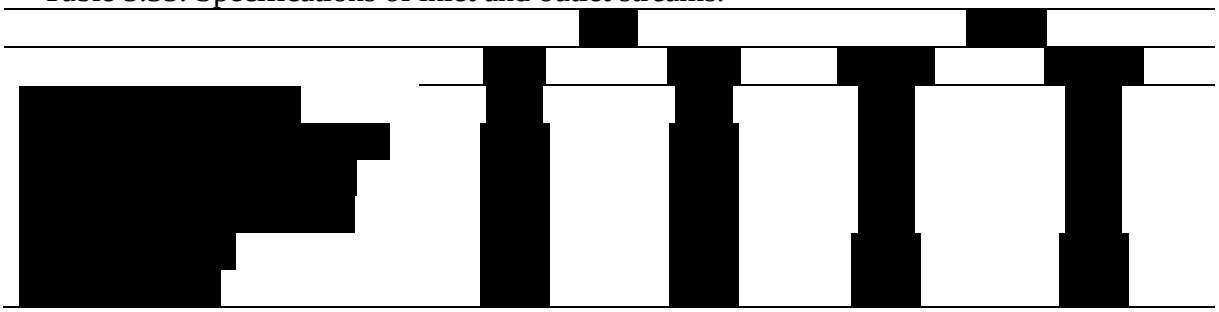
Figure 5.23. Representation of valve states during the rinse step.

4. Desorption (DE): In this step, all previously open valves are closed, and the product valve is opened. The pressure in the column is reduced until the ethylene is desorbed from the activated carbon.

Figure 5.24. Representation of valve states during the desorption step.

Once the operation of the adsorption system has been explained, all the mentioned elements must be specified. As previously stated, in this simulation the parameter fixed for all feed and product elements is pressure, making the flow rate a degree of freedom. The specifications for the feed blocks (FEED, RINSE) and product blocks (OFF-GAS, PRODUCT) are shown below.

Table 5.35. Specifications of inlet and outlet streams.



During the desorption stage, an initial target pressure of proposed. However, during the simulation, it was observed that under these conditions, the column was unable to desorb properly, and numerical errors arose, resulting in negative outlet flow rates and the interruption of the calculation. The same issue occurred when varying the adsorption pressure, as attempts were made to simulate the process at without success. In all cases, the column remained saturated and failed to desorb correctly, preventing stable cycle completion.

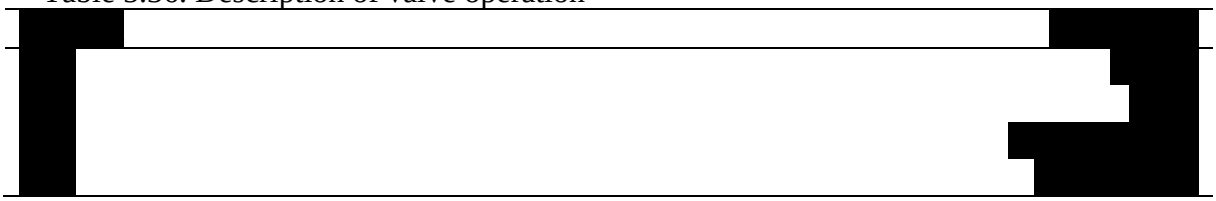
To enable effective desorption of the bed, the final pressure of this stage was reduced to . While this adjustment did not completely resolve the simulator's numerical issues, it did allow for full desorption of the bed and completion of the cycle. However, this modification

has a significant implication: operating the desorption stage below atmospheric pressure means that the process is no longer a strict PSA (Pressure Swing Adsorption) but becomes a VPSA (Vacuum Pressure Swing Adsorption). This implies that, in a real installation, a vacuum system would be required.

It should be noted that the design and sizing of the vacuum equipment fall outside the scope of this project, although it is considered a key technical requirement for replicating the operating conditions used in the simulation. This stage proved particularly challenging during modelling, and its impact on process performance is discussed in detail in the results section.

Another factor to take into account is the opening or closing of the valves and their different operating modes, which are described in Table 5.36.

Table 5.36. Description of valve operation

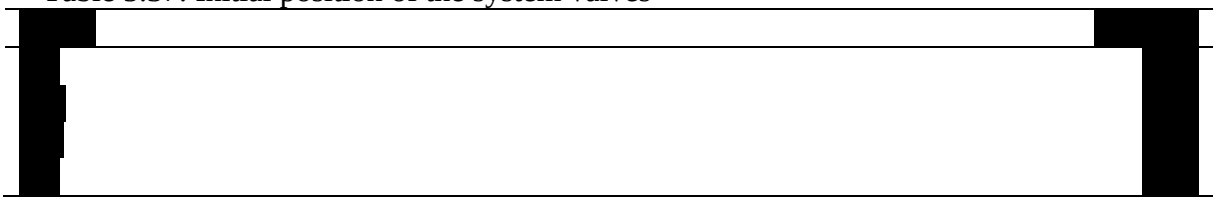


In this work, valve opening will be controlled using position 2. This mode in Aspen Adsorption software corresponds to valve which operates under the assumption that the molar flow through it is linearly related to the pressure drop across the valve, as shown in Equation 5.14.

$$F = Cv\Delta P \tag{5.14}$$

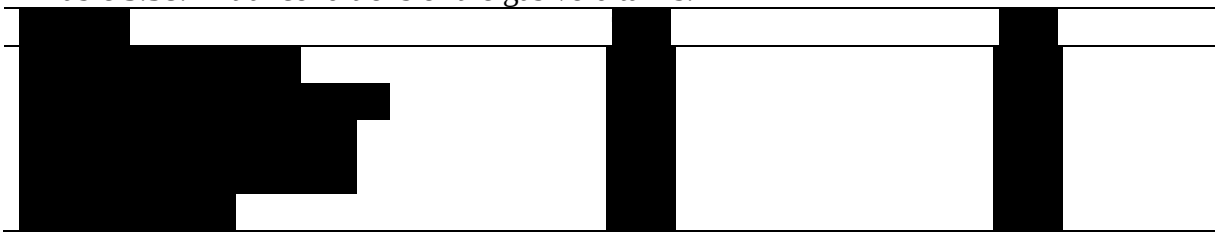
As a summary, the initial configuration of the valves is presented, which will open or close depending on the stage of the cycle in which the column is operating.

Table 5.37. Initial position of the system valves



In addition, the gas void tanks must be initialized, in this simulation are called TD1 and TD2. They act as pressure anchors between active blocks, such as the valves and the column itself. Each active block consists of a set of differential equations, and these tanks act as passive elements to transfer variables from one set of equations to another.

Table 5.38. Initial conditions of the gas void tanks.



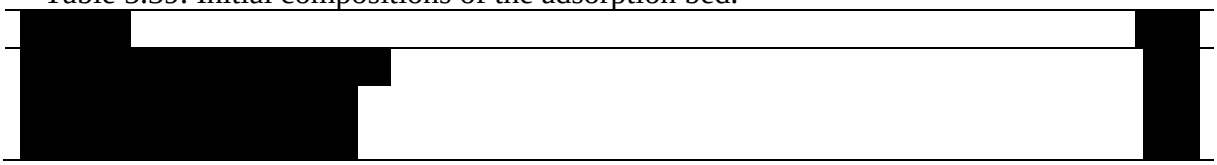
As shown in Table 5.38, it is necessary to define the initial state of the system, including the composition within the void volumes connected to it. In this work, it has been assumed that both the column and the tanks, as well as the void spaces, initially contain only nitrogen.

This condition sets the mole fraction of the components in the unloaded volumes and in the first node of the bed. This assumption is based on the fact that nitrogen is an inert component and is commonly used as a purge gas during startup conditions. Although nitrogen shows some affinity for the adsorbent, as seen in the equilibrium isotherms, its adsorption capacity is moderate compared to that of ethylene, allowing it to be used as the initial gas in the bed without significantly affecting the system behaviour.

Moreover, this configuration helps to stabilize and facilitate the convergence of the system.

The initial bed compositions are shown in Table 5.39.

Table 5.39. Initial compositions of the adsorption bed.



Once the full simulation scheme has been established, a function in Aspen Adsorption software called Cycle Organizer is added. This block facilitates programming the sequence, duration, and assignment of steps within the simulation. Within this module, the duration of each step is defined, along with the valve positions and flow coefficients for each stage.

Table 5.40. Duration of each step.

[redacted]

Table 5.41. Valve opening settings.

[redacted]

6. RESULTS AND DISCUSSION

7. ENVIROMENTAL AND ECONOMIC EVALUATION

8. CONCLUSIONS

The present work has addressed the design and evaluation of a vacuum pressure swing adsorption (VPSA) unit aimed at the treatment and valorisation of a gaseous residual stream generated at the top of the ethylene/propylene distillation column. This stream, composed predominantly of ethylene along with nitrogen and hydrogen, contains non-condensable components which, under normal operating conditions, are purged from the system and sent to flare or internal combustion, resulting in a net loss of valuable raw material.

The proposed strategy consists of recovering ethylene through its selective adsorption on a solid bed, with the objective of reducing emissions and improving the overall efficiency of the production process. A detailed characterization of the feed stream to the VPSA unit was initially carried out. [redacted]

The VPSA unit design is based on the use of activated carbon as adsorbent selected for its high selectivity towards ethylene under low-pressure conditions. The proposed cycle consists of adsorption, blowdown, rinse with pure ethylene, and desorption steps, which allow for efficient recovery of the target component and regeneration of the adsorbent bed.

Dynamic simulation of the system was performed using Aspen Adsorption software, considering multicomponent behaviour and competitive adsorption effects. The results demonstrate stable operation under the defined conditions, with preliminary results in the desorption step showing an ethylene recovery of [redacted]% and a product purity of [redacted] mol%. Analysis of the transient cycle profiles shows that the selected rinse strategy is effective for adsorbent regeneration, significantly reducing ethylene losses.

From a technical standpoint, the implementation of this unit enables the effective separation of non-condensable components, preventing their loss and improving ethylene recovery.

It is worth noting that one of the main challenges encountered during the development of the project was the difficulty in obtaining reliable data to define the multicomponent adsorption equilibrium, particularly under vacuum conditions and for mixtures with high ethylene content. Available literature data are limited and often refer to binary systems or operating conditions different from those considered in this study. Therefore, a logical next step in the further development of the project would be to establish direct contact with adsorbent manufacturers or suppliers in order to obtain experimental data specific to the system under evaluation. Such collaboration would allow for a more accurate calibration of the adsorption model, improve the reliability of simulations, and ultimately optimize the design of the proposed VPSA process.

Although it lies outside the scope of the present project, it is important to note that, depending on the adsorption isotherms and updated data provided by the supplier in future stages, it may become necessary to apply vacuum during the desorption step in order to achieve efficient regeneration of the adsorbent. In such a case, reintegration of the recovered ethylene into the reaction section would require a dedicated compression system. A piston compressor would likely be the most suitable technology, given the relatively low flow rate and the need to reach the operating pressure of the polymerization reactor. This additional equipment would need to be incorporated into the system design to ensure continuous and efficient reuse of the recovered ethylene as a raw material.

Regarding the non-recoverable components, it has been determined that, since there is currently no specific separation system in place for the nitrogen and hydrogen present in the stream, these gases will be sent to the flare. This approach enables the safe management of non-condensable gases once the ethylene desorption process is complete, preventing their accumulation in the system and ensuring compliance with operational safety standards.

Additionally, a preliminary assessment of the environmental and economic impact of the project has been conducted. The recovery of ethylene prevents its combustion, which translates into an estimated CO_2 emission reduction of approximately [redacted] tons per year. From an economic standpoint, the valorisation of this stream reduces raw material loss and consequently improves the profitability of the process, avoiding the cost associated with CO_2 emissions, estimated at €[redacted] annually.

In conclusion, the integration of a VPSA unit for the treatment of the top residual stream from the ethylene/propylene distillation process has proven to be technically feasible and represents a potential improvement in operational efficiency, sustainability, and emission reduction. Although a detailed economic analysis has not been carried out, the proposed concept shows favourable indicators that may justify its further development. This project aligns with the industry's current objectives of enhancing resource circularity and progressively decarbonizing the petrochemical sector.

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ANNEXES

A. ANNEXES