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Master of Science in Petroleum Engineering

Process modelling of methanol synthesis via membrane-based carbon capture, alkaline electrolysis and catalytic hydrogenation

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To mom and dad,

I owe you everything.

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ABSTRACT

Methanol plays an important role in the energy and chemistry sectors, since it can be directly used as fuel and energy carrier or involved as precursor in the production of chemicals like dimethyl ether (DME) or olefins (e.g., ethylene and propylene). Methanol demand shows an increasing trend which is fulfilled by involving large scale production facilities.

Nowadays methanol is mainly produced from the catalytic conversion of a syngas (i.e., a mixture of hydrogen, carbon monoxide and carbon dioxide) obtained via methane reforming or coal gasification. As an alternative, green/renewable methanol can be produced when hydrogen is obtained via water electrochemical splitting (electrolysis) by exploiting surpluses from intermittent renewable electricity. H_2 can react with carbon dioxide to produce methanol as a part of Power-to-X pathways. CO_2 can be obtained through carbon capture from industrial flue gases or as a by-product of biogas-to-biomethane upgrading.

In this work, a process modelling for the catalytic hydrogenation of carbon dioxide into methanol was carried out. A CO_2-rich stream is obtained through biogas upgrading by means of membranes, it is mixed with hydrogen produced via low-temperature alkaline electrolysis and then sent to a catalytic reactor for methanol synthesis.

For this purpose, two different models have been developed. The first one consists of a MATLAB code simulating a set of membranes for the biogas upgrading and to obtain a by-product gaseous stream with a sufficiently high amount of carbon dioxide. The CO_2-rich stream is the input of a second model developed in ASPEN Plus environment, where it is mixed with hydrogen from alkaline electrolysis. The reacting mixture is sent to a Plug Flow Reactor (PFR) incorporating the kinetic model for methanol synthesis. The obtained gas is sent to an upgrading section where methanol is separated from water and unreacted gases. Overall energy efficiency of the whole process was carried out, accounting for the produced methanol energy content as well as electric and thermal energy demand.

An experimental campaign for the acquisition of data to evaluate the permeability of membranes both to CO_2 and CH_4 was carried out within the CO_2 Circle Lab at Environment Park (Turin).

CHAPTER 1: INTRODUCTION

Fossil fuels have long been the primary source of energy for many decades, but they are progressively being replaced by renewable energies for several reasons, in first place in terms of environmental concerns: fossil fuels are a significant source of greenhouse gas emissions, which contribute to climate change and its associated impacts. As such, there is growing concern about the environmental impacts of fossil fuels, and renewable energies are seen as a cleaner and more sustainable alternative. In addition in recent years renewable energies have become increasingly cost-competitive with fossil fuels, particularly in the electricity sector. The cost of solar, wind, and other renewable technologies has declined significantly, making them more affordable and attractive to consumers and businesses. Another aspect is surely related to technological advances in renewable energy technologies, such as improvements in solar and wind power generation and energy storage, have made these technologies more efficient and reliable, enabling them to compete with fossil fuels on a level playing field.

Dependence on fossil fuels can create energy security concerns, as countries can be vulnerable to supply disruptions, price volatility, and geopolitical tensions. Renewable energies, on the other hand, are domestic and more resilient, providing a secure source of energy for countries and reducing their dependence on foreign energy sources.

Alternative fuels refer to any fuel that is not derived from traditional fossil fuels. Examples include biodiesel, ethanol, hydrogen,, and electricity. Alternative fuels are being developed and used to reduce dependence on fossil fuels, improve energy security, and reduce greenhouse gas emissions. However, the adoption of alternative fuels has been limited by factors such as infrastructure development, vehicle compatibility, and cost. Reducing reliance on fossil fuels with alternative fuels can be achieved through several strategies.

Governments can incentivize the production and distribution of alternative fuels, such as ethanol and biodiesel, by providing subsidies and tax credits for their production and use.

Infrastructure such as fueling stations, charging stations, and pipelines need to be developed to support the use of alternative fuels. Governments and private companies can invest in developing this infrastructure to encourage the use of alternative fuels.

Energy efficiency measures, such as building retrofits, efficient lighting and appliances, and public transportation, can reduce the demand for fossil fuels and help shift towards more sustainable energy sources.

Research and development can help to improve the efficiency and affordability of alternative fuels, making them more competitive with traditional fossil fuels.

Policies such as carbon pricing or emissions standards can help to reduce the environmental impact of fossil fuels and encourage the adoption of alternative fuels.

1.1. Methanol solution

Right in this direction **methanol** is a fuel that can be easily produced from renewable sources and is easier to transport and store than natural gas or hydrogen. Additionally, methanol has a high energy content and can be used in internal combustion engines without significant modifications. Methanol is relatively inexpensive to produce compared to other fuels and chemicals, making it an attractive option for a wide range of applications.

Methanol can be produced from a variety of sources, including natural gas, coal, and biomass. Here are some of the different ways methanol can be produced:

Steam methane reforming: This is the most common method of producing methanol and involves converting natural gas or methane into synthesis gas (a mixture of hydrogen and carbon monoxide) through a high-temperature steam reaction. The synthesis gas is then converted to methanol using a catalyst.

Coal gasification: Methanol can also be produced by gasifying coal, which involves heating coal in the presence of oxygen and steam to produce a synthesis gas that can be converted to methanol.

Biomass gasification: Methanol can be produced from biomass through gasification, which involves heating organic materials such as wood chips or agricultural waste in the presence of oxygen and steam to produce synthesis gas.

Carbon dioxide capture and utilization: Methanol can be produced by capturing carbon dioxide emissions from industrial processes or the atmosphere and combining it with hydrogen to produce methanol through a process known as carbon capture and utilization (CCU).

Electrochemical reduction of carbon dioxide: Methanol can also be produced through the electrochemical reduction of carbon dioxide, using renewable electricity and catalysts to convert carbon dioxide into methanol.

1.2. Carbon Capture and Utilization (CCU)

As mentioned before, carbon capture and utilization (CCU) is a process that involves capturing carbon dioxide emissions from industrial processes or the atmosphere and using them as a feedstock to produce valuable products, such as chemicals, fuels, or building materials. One of the advantages of CCU is that it can create a market for carbon dioxide emissions, making carbon capture more economically viable. CCU can also reduce the environmental impact of industrial processes by reducing carbon dioxide emissions and by using waste materials as feedstocks. Moreover, CCU can contribute to the circular economy by reusing waste materials and reducing the dependence on fossil fuels.

Figure 4.1: Carbon Capture and Utilization (CCU) outline

CCU technologies can use different feedstocks to produce a variety of products. For example, carbon dioxide can be converted into methanol or other chemicals through chemical reactions with hydrogen or other feedstocks. Carbon dioxide can also be used as a building block to produce plastics, such as polyurethanes or polycarbonates.

Directly related to the present thesis work, methanol is produced from carbon dioxide and hydrogen through a process known as carbon dioxide reduction or **carbon dioxide hydrogenation** where CO2 is initially captured from methane-rich biogas stream using membrane separation, in parallel hydrogen stream is produced from water using electrolysis. The captured carbon dioxide and hydrogen gas are then reacted over a catalyst at high temperatures and pressures to produce methanol.

The chemical reaction for the production of methanol from carbon dioxide and hydrogen can be represented as follows (it will be explained more in detail later):

$$CO_2 + 3H_2 \rightarrow CH3OH + \ H_2O$$

This process not only reduces carbon dioxide emissions but also produces a valuable chemical product, methanol, that can be used as a fuel or feedstock for various industries. The production of methanol from carbon dioxide and hydrogen is still in the development phase, and there are several challenges that need to be addressed to make the process more efficient and cost-effective. These include improving catalyst performance, reducing energy consumption, and optimizing process conditions.

1.3. Methanol economy

A necessary transition from a fossil-based economy to one based on renewable sources is underway, nevertheless the renewable energy sources sore point, such as wind and solar is represented by intermittency problems as they rely on weather conditions and time od the day. To offset this, if the goal is to achieve a major renewable penetration, energy storage solutions are more and more necessary. Water electrolysis for hydrogen production from excess renewable electricity is one of the most attempted options with very high capacity and fast response time for grid-balancing purposes.

The concept of a "**methanol economy**" involves using methanol as a fuel and energy carrier instead of traditional fossil fuels such as oil and coal. In a methanol economy, methanol would be produced from renewable sources such as biomass or solar energy, and used for power generation in vehicles, power plants, and industrial facilities. Methanol represents an important carbon-neutral electrofuels when produced from hydrogen via electrolysis and CO_2 from the atmosphere.

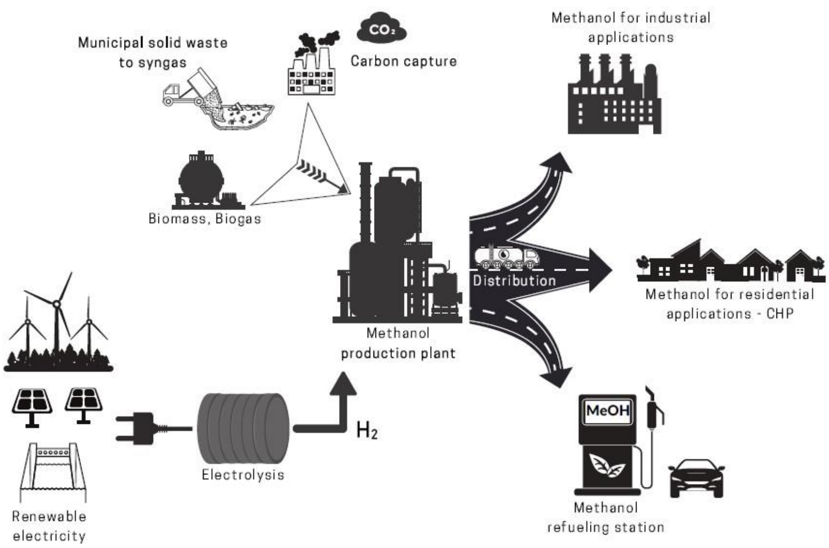


Figure 1.2: Methanol economy scheme

This concept has been proposed as a potential solution to reduce dependence on fossil fuels and mitigate climate change, as methanol can be produced using renewable energy sources and has a lower environmental impact than fossil fuels. However, there are still technical and economic challenges to overcome in order to make the methanol economy a widespread reality.

CHAPTER 2: MEMBRANE SEPARATION

Separating gaseous mixtures is a matter of interest for multiple reasons. As first a pure gas could be required for industrial or medical purposes so impurities must be eliminated while in terms of safety the separation of dangerous mixtures can prevent the formation of toxic or explosive combinations of gases. Usually, the separation is aimed to only one of the components, for example nitrogen, oxygen and carbon dioxide have more applications and they result more valuable. Actually, to prevent the environment it could be asked to separate dangerous pollutant to avoid increasing emissions.

Nowadays many techniques have been developed which are capable of separating gases depending on composition and properties of the gases and the principal ones are here listed. Distillation is a process of separating the components of a mixture based on their boiling points. The mixture is heated, and the components with lower boiling points vaporize and are collected separately. This method is useful when the gases have different boiling points. On the other way when the gases have similar boiling points, we talk about cryogenic separation which is a process of separating gases based on their boiling points at low temperatures. The gases are cooled to very low temperatures, and the components with lower boiling points condense and are collected separately. In a physical or chemical approach, adsorption is a process of separating gases based on their ability to be adsorbed onto a solid surface. The gases are passed over a material that has a high surface area and a high affinity for the gas. The gas is adsorbed onto the surface, and the remaining gas is collected. An evolution of adsorption could be pressure swing adsorption (PSA) is based on gases ability to be adsorbed at different pressures. The gas mixture is passed over a material that adsorbs one gas more strongly than the other. The pressure is then changed, and the more strongly adsorbed gas is released while the other gas remains adsorbed. This method is useful when the gases have different adsorption characteristics. In membrane separation process gases are separated based on their ability to pass through a semi-permeable membrane. The membrane allows some gases to pass through while others are retained. Membrane separation is the method we will use for CO2 separation from biomethane into a biogas stream.

2.1. Diffusivity theory

Diffusivity theory is a branch of science that deals with the study of how molecules move and spread in different mediums, such as liquids, gases, and solids. The theory is based on the principles of mass transfer, which involve the movement of a substance from a region of high concentration to a region of low concentration.

In diffusivity theory, the diffusion coefficient or diffusivity is a key parameter that describes the rate of movement of molecules in a medium. The diffusion coefficient is influenced by factors such as the size and shape of the molecules, the temperature, the pressure, and the viscosity of the medium.

Diffusivity theory finds applications in a wide range of fields, including chemical engineering, materials science, physics, biology, and environmental science. It is used to model the diffusion of substances in different systems, such as the transport of pollutants in the environment, the diffusion of nutrients in biological tissues, and the diffusion of drugs across cell membranes.

Diffusivity theory and Fick's law are closely related concepts in the field of mass transfer. Fick's law is a fundamental law that describes the diffusion of a substance in a medium. It states that the rate of diffusion is proportional to the concentration gradient, and the constant of proportionality is the diffusion coefficient or diffusivity.

Mathematically, Fick's first law can be expressed as:

$$J = -D\left(\frac{dC}{dx}\right)$$

where J is the flux of the substance, D is the diffusion coefficient or diffusivity, C is the concentration of the substance, and x is the distance. The negative sign indicates that the flux is directed from higher concentration to lower concentration.

Diffusivity theory provides a more detailed understanding of the factors that influence the diffusion coefficient. It takes into account the size and shape of the molecules, the temperature, the pressure, and the viscosity of the medium. By incorporating these factors, diffusivity theory enables us to predict the diffusion coefficient for a given substance in a given medium.

In summary, Fick's law is a fundamental law that describes the diffusion of a substance, and diffusivity theory provides a framework for understanding the factors that influence the diffusion coefficient. Together, these concepts provide a comprehensive understanding of mass transfer in different systems.

A separation membrane can be located within the framework of diffusivity theory by considering its role in controlling the diffusion of molecules or particles between two regions. A separation membrane is a thin layer of material that is selectively permeable, meaning that it allows certain molecules or particles to pass through while blocking others.

The permeability of a separation membrane is determined by its properties, such as its pore size, surface charge, and chemical composition. The separation membrane can be designed to selectively allow the diffusion of certain molecules or particles, while blocking others based on their size, charge, or chemical properties.

By combining the principles of diffusivity theory and the properties of the separation membrane, we can predict and control the diffusion of substances across the membrane. This has practical applications in a variety of fields, such as water treatment, gas separation, and biomedical engineering. For example, in water treatment, separation membranes can be used to remove impurities and contaminants from water by selectively allowing the diffusion of certain ions or molecules.

2.2. Process and design

Membrane separation is a process which saw its interest increasing during years. Although there are many types of processes and principles related to several prototypes and models the only thing that is sure is the presence of the membrane which is typically made of polymers, ceramics, or metals, and can be designed to be porous or non-porous.

One of the advantages of membrane separation technology is that it is a cost-effective and energy-efficient process compared to traditional separation methods such as distillation or absorption. It also does not require any chemicals or solvents, making it a more environmentally friendly process. However, he separation efficiency is highly dependent on the membrane properties, and the membranes can be easily fouled by impurities in the gas stream. Additionally, the process may not be suitable for separating gases with similar molecular sizes or properties.

The characteristic of this process consists in the gaseous mixture passing through a membrane that selectively allows certain molecules to pass through while blocking others.

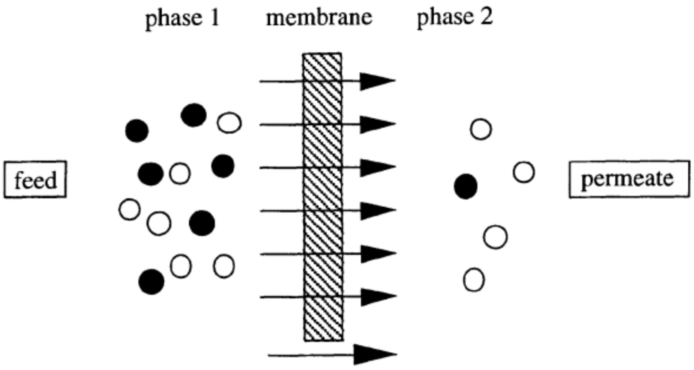


Figure 5.1: Schematic representation of a membrane functioning

On the left (phase 1) we see the **feed** or upstream side phase while on the right (phase 2) is the **permeate** or downstream side. Separation between them is achieved thanks to the membrane ability to transport one component from the feed mixture more readily than any other component and this concept takes the name of selective permeation.

In order to apply membranes on a technical scale, large membrane areas are normally required. The smallest unit into which the membrane area is packed is called a **module**.

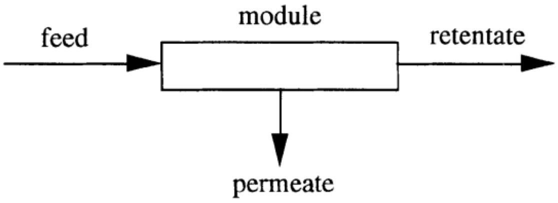


Figure 2.2: Simple design of a module

When the feed passes through the membrane it is divided into a permeate and a retentate stream with different molar fractions and concentrations. This process is generally realized in a cross-flow mode that means there will be a feed stream that will move parallelly to the membrane surface and its composition will change accordingly to the distance traveled in the module. There are many possible configurations for cross-flow operations:

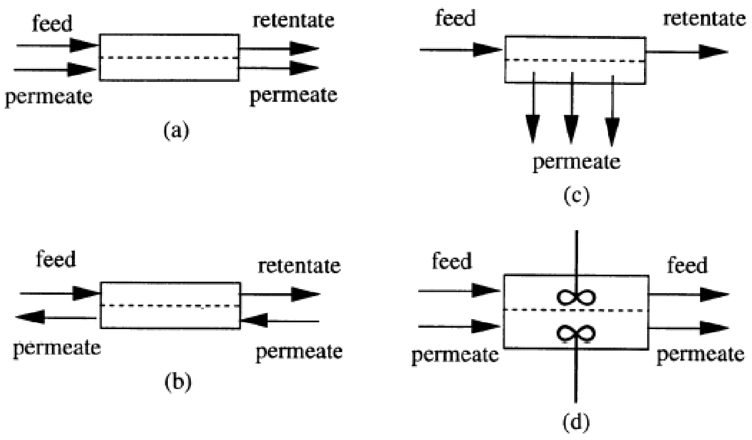


Figure 2.3: Different cross-flow models: (a) co-current; (b) counter-current; (c) cross-flow; (d) perfect mxing

Often the single-stage design does not guarantee the purity or the quality expected so the permeate or the retentate can be treated in a second stage and this configuration is called **cascade**.

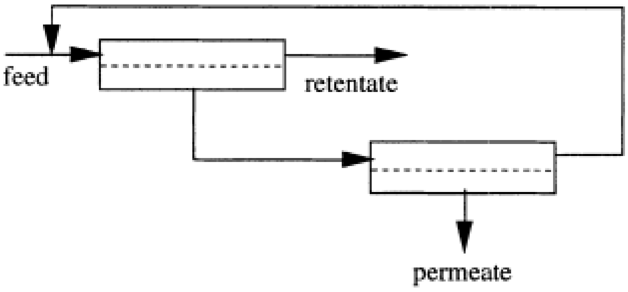


Figure 2.4: Scheme of a two-stage module in cascade

2.3. Membrane types

There are several types of separation membranes, each with different properties and applications. Some common types of separation membranes include:

Reverse osmosis membranes are thin, semipermeable membranes that are used to remove dissolved salts, minerals, and other impurities from water. They work by applying pressure to a solution to force water molecules through the membrane, while blocking the passage of larger molecules and particles.

Nanofiltration membranes are like reverse osmosis membranes but with larger pore sizes that allow the passage of some ions and molecules while retaining others. They are often used for desalination, as well as for separating organic and inorganic compounds. Ultrafiltration membranes have even larger pore sizes than nanofiltration membranes and are used for separating macromolecules, such as proteins and viruses, from smaller molecules and ions.

Microfiltration membranes have even larger pore sizes than ultrafiltration membranes and are used for separating suspended solids, bacteria, and other particles from liquids.

Gas separation membranes are used for separating gases, such as nitrogen and oxygen, based on their size and solubility. They are often used in industrial applications such as natural gas processing, hydrogen purification, and carbon dioxide capture. Electrodialysis membranes are used for separating ions from solutions based on their charge. They work by applying an electric field across a series of membranes to selectively remove ions from the solution.

Overall, the choice of separation membrane depends on the specific application and the properties of the substances being separated. The type of membrane selected will impact factors such as the separation efficiency, energy consumption, and overall cost of the separation process.

2.4. Polymeric membranes

For our treatment we deal with **polymeric membranes** which are thin films made from synthetic or natural polymers that are commonly used for separation and purification of gases or liquids. They can be produced in various forms, including flat sheets, hollow fibers, and spiral-wound modules.

Polymeric membranes are popular for their low cost, high flexibility, and easy processing compared to other separation techniques such as distillation or adsorption. They are also highly tunable in terms of selectivity and permeability, making them useful for a wide range of applications.

Polymeric membranes work based on the principle of selective permeation, where a driving force such as pressure or concentration gradient is applied across the membrane to separate molecules based on their size, shape, and affinity towards the membrane material.

Polymeric membranes are widely used in the separation of gases such as hydrogen, nitrogen, oxygen, and carbon dioxide. They are also used for the purification of water and other liquids.

2.5. Parameters and equations

Process parameters must be designed in order to fully characterize the membrane behavior. For our purposes we will describe the complete mixing model parameters.

As first it is important to state that isothermal conditions and negligible pressure drop in the feed stream and permeate stream are generally assumed as also the effects of total pressure of the gas are negligible. The permeability of each component is assumed constant.

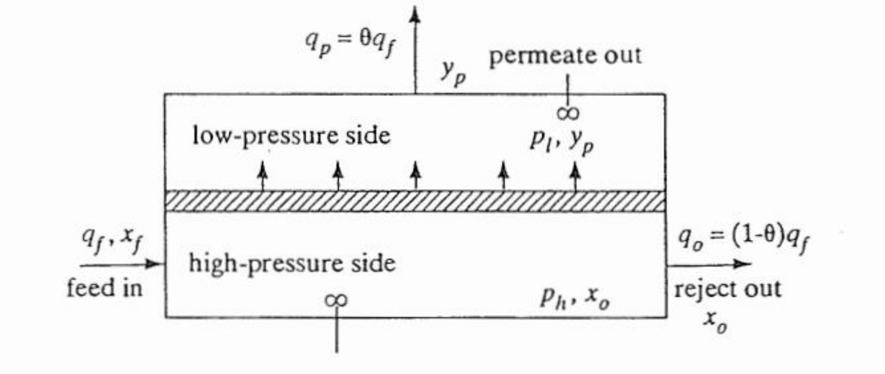


Figure 2.5: Process parameters for complete mixing case

The feed enters the system with a molar flow rate q_f and, if we hypothesize a mixture of A and B components, y_p and x_o respectively the molar fraction of A in permeate and in retentate section. x_f is the mole fraction of A in the feed. The overall material balance is:

$$\boldsymbol{q_f = q_p + q_o} \tag{1}$$

To define the total flowrate of permeate and retentate we introduce a parameter called **recovery R** (also **θ**) so we can define $q_p = q_f * R$ and $q_o = q_f * (1 - R)$. This parameter explains how much is the quantity of the feed that penetrates the membrane and has an economic importance.

The rate of permeation of component A is the related to its **permeability** which is the ability of a gas to diffuse through a membrane when the pressure of each side is different and is measured in Barrer ($1\ barrer = 10^{-10}\ \frac{cm^3_{STP}*cm}{cm^2*s*cmHg}$).

The relationship is:

$$\boldsymbol{\frac{q_A}{A_m} = \frac{q_p y_p}{A_m} = \left(\frac{P_A}{l}\right)(p_h x_o - p_l y_p)} \tag{2}$$

where l is the membrane thickness [cm], A_m is the membrane area, p_h is the total pressure in the high-pressure side (feed) [cmHg], p_l is the total pressure in the low-pressure side (permeate) [cmHg]. β is the ratio between the high and the low pressure.

For the component A and overall material balance results in:

$$q_f x_f = q_o x_o + q_p y_p \tag{3}$$

Readapting the different equations, we can solve for the membrane area obtaining:

$$A_m = \frac{R q_f y_p}{(P_A/l)(p_h x_o - p_t y_p)} \tag{4}$$

The last relevant parameter is for sure the **selectivity** of the membrane which refers to the ability of the membrane to separate one gas from another. It is typically expressed as the ratio of the permeability of one gas to another gas (for example, the permeability of CO2 to CH4). A higher selectivity means that the membrane is better at separating the two gases. Selectivity is defined as:

$$\alpha = \frac{P_A}{P_B} \tag{5}$$

2.5.1. Steady-state permeation

Steady-state permeation of gas refers to the continuous flow of a gas through a permeable membrane under constant conditions, such as temperature and pressure. The rate of steady-state permeation can be determined experimentally by measuring the amount of gas that passes through the membrane over a specific period of time, under controlled conditions. This information can be used to optimize the design and operation of gas separation systems, including those used in gas processing, chemical production, and environmental monitoring.

If we consider the x-direction as the preferential direction for a one-dimensional flux of gas A through the membrane, this flux can be expressed thanks to the Fick's law:

$$N_A = -D\frac{dC_A}{dx} + w_A(N_A + N_P) \tag{6}$$

rearranged for the flux of gas A:

$$N_A = -\frac{D}{1-w_A}\frac{dC_A}{dx} \tag{7}$$

where:

D is the gas diffusion coefficient in the film

C_A is the local concentration of dissolved gas

w_A is the weight fraction of gas A in the film

N_p is the flux of the membrane, which is typically taken to be zero.

It is possible to give a new definition for the permeability of the gas component A through the membrane:

$$\boldsymbol{P_A = \frac{N_A\, l}{p_h - p_l}} \tag{8}$$

Combining the two equations before and integrating from x = 0 (C = C2) to x = l (C = C1), the result is:

$$\boldsymbol{P_A = \ D_A \frac{C_2 - C_1}{p_h - p_l}} \tag{9}$$

where D_A is the concentration-averaged effective diffusion coefficient in the range C1–C2:

$$\boldsymbol{D_A = \frac{1}{C_2 - C_1} \int_{C1}^{C2} \frac{D}{1 - w_A} dC} \tag{10}$$

and, furthermore, D_{eff} is defined as the local effective diffusion coefficient:

$$\boldsymbol{D_A = \frac{1}{C_2 - C_1} \int_{C1}^{C2} D_{eff}\, dC} \tag{11}$$

A classic experimental situation is, for the sake of simplicity, to assume that le pressure in permeate site is much smaller than the feed pressure as also the $C_1 << C_2$. That's why measuring the average gas diffusivity could present difficulties so from the measurement of permeability and solubility we use a relationship that directly links these due parameters with the diffusivity so we state that:

$$\boldsymbol{P_A = D_A S_A} \tag{12}$$

defining S_A as the solubility of component A into the membrane.

Therefore, by measuring the gas permeability and solubility at the high pressure of the system, it's possible to calculate the average gas diffusivity D_A.

Equation (5) can now be reformuled using the relation between selectivity and solubility of the two components:

$$\boldsymbol{\alpha_{A,B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} = \alpha^D_{A,B} \alpha^S_{A,B}} \tag{13}$$

where $\alpha^D_{A,B}$ takes the name of **mobility** while $\alpha^S_{A,B}$ is called **sorption**. Mobility is > 1 if one if one component is higher than the other one while sorption is greater than 1 if one component is more condensable than the another.

2.5.2. Time-lag method

The second Fick's law explains the behaviour of the penetrant concentration as a function of time and position:

$$\frac{dC}{dt} = \frac{d}{dx}\left(D_{eff}\frac{dC}{dx}\right) \tag{14}$$

The solution is closely dependent on initial and boundary condition, furthermore the concentration could depend on the diffusion coefficient. Trying to simplify the calculation, from Crank and Park analysis it's possible to assume the diffusion coefficient as constant even if it is dependent on concentration, the only limitation is that D_{eff} is assumed different from the average value. Once it is assumed constant its evaluation is possible by using a permeation method called **time-lag method** which assumes zero concentration in the initial condition ($t = 0$) so the amount of penetrant Q_t that diffuses in the membrane is:

$$\frac{Q_t}{l\,c_i} = D\frac{t}{l^2} - \frac{1}{6} - \frac{2}{\pi}\sum\frac{(-1)^n}{n^2}\exp\left[-\frac{D\,n^2\pi\,t}{l^2}\right] \tag{15}$$

with c_i that represents the concentration on the feed side and n must be an integer number.

The behaviour of the flow of penetrant is described in the figure below, as time tends to infinite the initial curved trend of the transient becomes linear as steady-state conditions are reached.

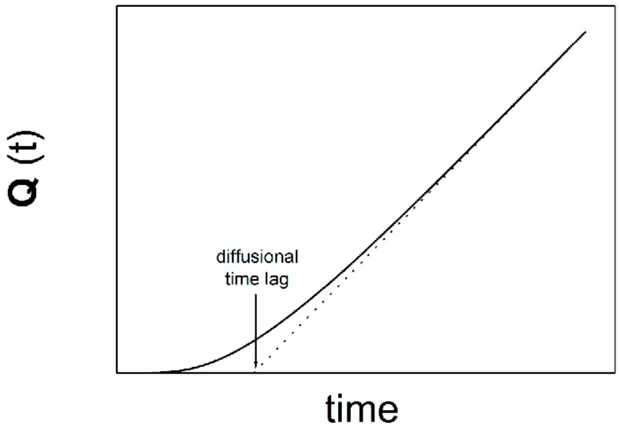


Figure 2.6: Penetrant flow rate behavior with respect to time

The flow of penetrant stabilizes at the value of:

$$Q_t = D\frac{c_i}{l}\left(t - \frac{l^2}{6D}\right) \tag{16}$$

And by intercepting this value with the x-axis of time we can define the **diffusion time-lag (θ)** that is in the denominator of the final equation for the diffusivity coefficient:

$$\boldsymbol{D} = \frac{\boldsymbol{l}^2}{\boldsymbol{6\theta}} \tag{17}$$

2.6. Membrane aging problem

Membrane separation aging is the process by which separation membranes degrade and lose their ability to efficiently separate substances over time. This can occur due to a variety of factors, such as exposure to harsh chemicals, high temperatures, and mechanical stresses.

One common cause of membrane separation aging is fouling, which occurs when particles and other impurities accumulate on the surface of the membrane. This can lead to reduced permeability, decreased separation efficiency, and eventually, membrane failure. Fouling can be caused by a variety of factors, such as the nature of the solution being treated, the properties of the membrane, and the operating conditions of the separation system.

Another factor that can contribute to membrane separation aging is chemical degradation, which occurs when the membrane is exposed to corrosive chemicals or high temperatures. This can lead to changes in the structure and properties of the membrane, resulting in reduced separation efficiency and increased risk of membrane failure.

To minimize the effects of membrane separation aging, it is important to carefully select the type of membrane for the specific application and to monitor the operating conditions of the separation system. This can include regularly cleaning the membrane to prevent fouling, optimizing the flow rate and pressure of the solution being treated, and using appropriate pretreatment processes to remove impurities before they reach the membrane.

2.7. Biogas upgrading

Biogas upgrading is the process of refining biogas to remove impurities, primarily carbon dioxide (CO2), and increase its energy content, typically by increasing its methane (CH4) concentration. Biogas is a renewable fuel that is produced through the anaerobic digestion of organic materials, such as agricultural waste, food waste, and sewage.

Biogas upgrading is essential for making biogas a viable fuel source for applications such as electricity generation, heating, and transportation. Upgraded biogas has a higher energy content, reduced impurities, and can be transported over longer distances through pipelines. Additionally, the process of upgrading biogas can also produce valuable byproducts, such as fertilizer or other chemicals.

Membrane separation uses a semi-permeable membrane to selectively remove impurities from biogas. Biogas is fed through a series of membranes that allow CH4 to pass through while retaining CO2 and other impurities. For our purpose the application that we will see in the next chapter will be exactly the opposite as on the permeate site we will have a CO2-rich stream while on the retentate side a stream containing high content of CH4 will be sent to the grid.

Membranes typical for biogas upgrading are made of polymeric materials such as polysulfone, polyimide or polydimethylsiloxane.

The numbers and the interconnection of applied membrane stages are not determined by the desired biomethane quality but by the recovery of the methane required and the specific demand for compression energy. The moderns upgrading plants with a more complex design offer a lot of methane recovery possibilities high with relatively low amount of energy. Multi-mode compressors have also been developed and have proven to be cost-effective. The pressure and speed of compressor operation are both controlled to provide the quality and quantity of the biomethane produced.

The application of this technology for biomethane production is advantageous if the plant capacity is not high, in addition the methane contained in the biomethane (95.0-99.0 vol%) is suitable for further use. Other specifics of this type of plant consists in biomethane stream directly used at delivery pressure without additional compression and heat demand of the biogas plant (partly) covered by the gas treatment of discharge. Additional chemicals and other consumables should be avoided.

CHAPTER 3: EXPERIMENTAL ACTIVITY

An experimental campaign for the acquisition of data to evaluate the permeability of membranes both to CO_2 and CH_4 was carried out within the CO_2 Circle Lab at Environment Park (Turin).

3.1. Permeation cell

A permeation cell is a device used to measure the rate of diffusion or permeation of a gas or vapor through a solid material, such as a membrane or film. The cell typically consists of two chambers separated by the material being tested. One chamber is filled with the gas or vapor to be measured, and the other chamber is kept at a constant pressure and monitored for any changes in concentration over time.

A silicon or Viton o-ring is often used to prevent gas leakage at the film edge from the upstream (i. e., high-pressure) to the downstream (i. e., low-pressure) side of the cell and to avoid gas exchange between the upstream portion of the cell and the exterior atmosphere.

The type of flow of the entering gas is radial from the centre of the film to the edge, then leaves the cell eliminating any possible trapped gas. Compared to the permeate gas flow rate the upper one at higher pressure is much higher in order to prevent difficulties in measurements, so a coherent choice is having the so called **stage cut (*Φ*)** similar to 1%:

$$\boldsymbol{\Phi} = \frac{\boldsymbol{Permeate\ flow}}{\boldsymbol{Feed\ flow}} \tag{18}$$

There’s a small difference in terms of value between the available area for gas diffusion and the real area of the film because the presence of the o-ring creates a contact area where diffusion doesn’t proceed. Furthermore, the o-ring would leave an imprint on the film. The inside diameter of the imprint is often used to calculate the active test area.

3.2. CO2-capture experimental set-up

The experimental data acquisition session was carried out in the CO2 Circle Lab (CCL) in Environment Park in Turin, Italy more precisely at the so-called CO2 capture system test bench.

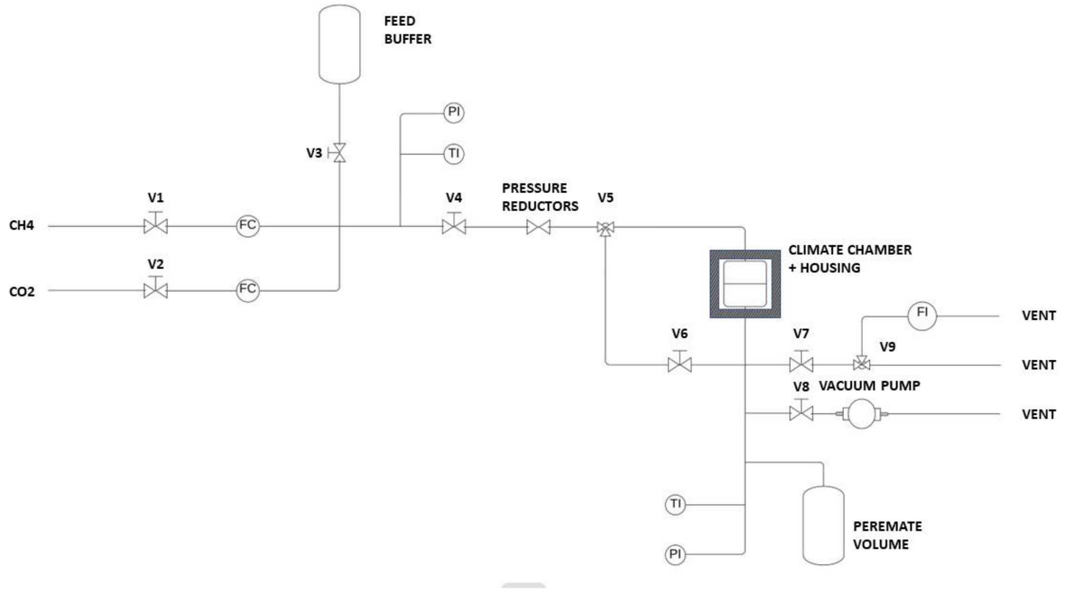


Figure 3.1: Schematic representation of the CO2 capture system test bench

This system permits the evaluation of diffusion parameters for N2, H2, CO2, CO, CH4 and O2 but for our purpose only CO2 and CH4 are tested. Their flows are controlled by two valves (V1 and V2) and two mass flow meters and controllers (FC). Valves permit different gases to flow into the system while FC components regulate the volume flowrate. A feed buffer is present after this first part of the system and its opening/closing set-up is regulated by valve V3. This collector has 1L volume. After a pressure and temperature indicators, V4 regulates the passage of the stream to two pressure reductors that adjust the outlet pressure while V5 is a three-way valve which can conduct to feed side, permeate side or both. Then we arrive to the climate chamber where the housing with the membrane are located, temperature can vary approximately between -20°C and 80°C. The two sides of the membrane can be isolated by valve V6 while a pressure indicator in the permeate site is able to read the pressure and acquire it, values are between 0 and 10 bars. Before leaving from the vent, the gas passes through V7 which is connected to the permeate side and a volumetric flowrate instrument (measures from 5 ml/min to 550 ml/min) and it can vent directly or passing through V9. Parallel to this line a vacuum pump guarantees possible evacuation of gases by decreasing pressure to $1 \cdot 10^{-4}$ bar.

There are two ways to acquire data: the closed volume configuration and the open system configuration, for our analysis the first one will be explained in detail.

It is important to underline that leakages in the permeate side are neglected as there is at least an order of magnitude with respect the permeate gas flowrate. 1.00 and 1.30 bar are respectively the initial and final experiment pressure in the permeate side.

Gas permeability is calculated from the following expression:

$$P_A = \frac{V_d\, l}{p_2 A\, R\, T}\left[\left(\frac{dp_1}{dt}\right)_{ss} - \left(\frac{dp_1}{dt}\right)_{leak}\right] \tag{19}$$

where:

V_d is the downstream volume $[cm^3]$;

l is the film thickness $[cm]$;

p2 is the upstream absolute pressure $[cmHg]$;

A is the film area available for gas transport $[cm^2]$;

R is the gas constant with value 0.278 $[\frac{cmHg\ cm3}{cm3(STP)\ K}]$;

T is absolute temperature $[K]$;

$\left(\frac{dp_1}{dt}\right)_{ss}$ and $\left(\frac{dp_1}{dt}\right)_{leak}$ are the steady- state rates of pressure rise$[\frac{cmHg}{s}]$ in the downstream volume at fixed upstream pressure and under vacuum, respectively.

3.2.1. Closed volume test

This test measures the permeate flux monitoring the pressure increase in a closed volume and pressure variation are acquired with a pressure transducer. As start procedure, any possible impurity is eliminated by creating vacuum conditions in the circuit then all the valves except for V1, V2 and V7 are opened. At this stage the pressure system is in the order of 10^{-3} bar. Following vacuum pump is disconnected and V8 and V4 are closed, V1 and V2 are opened based on the gas we want to test. The flowrate is set with the FC. We register an increase of pressure in the feed reservoir. Then pressure reductors are closed, V4 is opened, and the outlet pressure of the reductors is set to be equal to the one designed for the feed of the membrane (from 2 to 10 bar). In order to set the feed pressure, during regulation V5 is set to send the gas both in the feed and permeate side, V6 is opened: pressure is read in the permeate pressure indicator. When the pressure indicator for permeate shows a value of pressure equal to the desired one the procedure for evacuating the permeate side through the vent starts: V6 is closed, V7 is opened and V9 is set do directly conduct the gas to the vent. When PI in the permeate side shows 0.99 bar, V7 is closed and V5 is set to send gas to the feed side only. Now the acquisition can start by saving permeate PI values in time. Acquisition should last until the change of pressure in time can be supposed linear and for our purpose the range is:

$$p_{perm} = 1.00\ bar + (0.03 \cdot \Delta p) bar \tag{20}$$

where p_{perm} is the pressure showed by permeate PI and Δp is the pressure difference between feed side and permeate side (this value ranged between 1 bar and 9 bar). 0.03 coefficient represents a compromise between acquiring enough data and having the supposed linear trend.

As soon as the acquisition is finished in order to start a new acquisition the permeate side must be evacuated so V7 and V9 are opened to let the gas to vent until the value of 0.99 bar that means closing V7. New acquisition can start by saving permeate PI values in time in another data file.

When another feed pressure needs to be set, V5 is set to send the gas both in the feed and permeate side and V6 is opened. When permeate PI shows the desired feed pressure, gas in the permeate side has to be evacuated through the vent: V6 is closed, V7 is opened and V9 is set to send the gas directly to VENT. When PI in the permeate side shows 0.99 bar, V7 is closed, V5 is set to send gas to the feed side only and a new acquisition can start.

3.2.2. Results for Matrimid membrane

The membrane used in the laboratory for the permeability evaluation is made by Matrimid 5218 polyimide (3,3’,4,4’-benzophenone tetracarboxylic dianhydride and diaminophenylindane). It is tested at a temperature of 20°C and the membrane has a thickness of 80 µm.

The results obtained are schematized in the following table:

CH4		CO2		SELECTIVITY	
Δp [bar]	P [barrer]	Δp [bar]	P [barrer]	Δp [bar]	Selectivity [-]
1	0.031018	1	2.790927	1	89.97819884
2	0.062676	2	2.938854	2	46.88979493
3	0.046388	3	2.827715	3	60.95836825
5	0.054517	5	2.817734	5	51.68512159
7	0.054929	7	2.922851	7	53.2110769

Table 3.1: Permeability and selectivity results for Matrimid membrane.

Values of permeability are calculated for different Δp between feed and permeate according to Eq. (19)

3.3. MATLAB model of the membrane

MATLAB is a programming and numeric computing platform used by millions of engineers and scientists to analyze data, develop algorithms, and create models.

Our purpose is to create a model that calculates composition, flowrates, total membrane area and compression consumptions of a membrane that separates a biogas stream into biomethane and carbon dioxide.

A bi-stage membrane in cascade is modelled according to the figure below, CO2 permeate flow of the first stage is sent to the second module and separated again from biomethane in order to obtain a higher separation. Two compressors before each stage increase pressure of the feed flow accordingly to the model request.

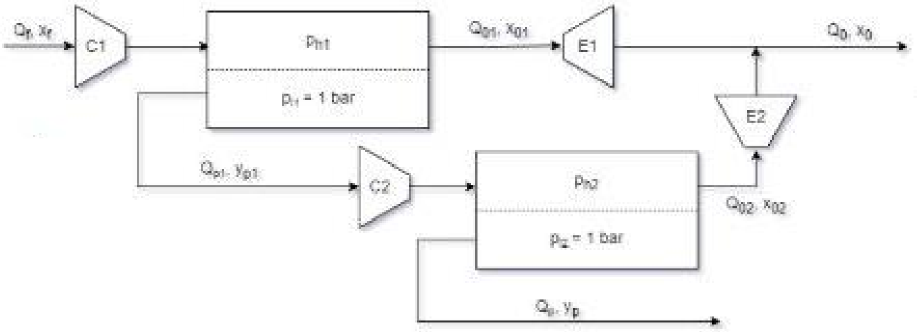


Figure 3.2: Schematic representation of a bi-stage membrane in cascade

Similar to the solution proposed in '*Transport processes and separation process principles*' book, this model defines three parameters called a, b and c for the direct evaluation of molar fraction of the component in the permeate:

$$a = \beta(P_B - P_A)$$

$$b = P_B\left(1 - x_f + Rx_f - \beta - \beta Rx_f\right) + P_A(\beta + x_f - Rx_f + \beta Rx_f)$$

$$c = P_B\left(\beta Rx_f - Rx_f\right) - P_A(x_f - Rx_f + \beta Rx_f)$$

it follows the evaluation of y_p:

$$y_p = \frac{-b+\sqrt{b^2-4ac}}{2a} \tag{21}$$

The model now exploits Eq. (1), Eq. (3) and Eq. (4), the y_p just evaluated and the input parameters which are $\left(p_h, p_l, P_A, P_B, q_f, x_f, R, l\right)$.

Not only membrane parameters but also electrical consumptions for both compressors are calculated (for the sake of simplicity expanders are neglected). To achieve this, the specific heat ratio has to be determined.

From *'Engineering and Chemical Thermodynamics'* appendix A.2, pag. 642, specific heat ratio for both CO2 and CH4 are evaluated starting from the general relationship:

$$\frac{c_p}{R} = A + BT + CT^2 + DT^{-2} + ET^3 \tag{22}$$

with:

T measured in $[K]$

$R = 8.314 \frac{J}{mol\ K}$

From table values it follows:

$\frac{c_{pCO2}}{R} = 5.457 + 1.045 * 10^{-3}T - 1.157 * 10^{5}T^{-2}$

$\frac{c_{pCH4}}{R} = 1.702 + 9.081 * 10^{-3}T - 2.164 * 10^{-6}T^{2}$

They are taken the mean values in the range 313.15-550 K for both the gases as we obtain:

$$\frac{c_{pCO2}}{R} = 5.90800$$

$$\frac{c_{pCH4}}{R} = 5.2079$$

The specific heat ratio in now calculated based on the formula for a mixture:

$$\gamma = \frac{\sum_i y_i c_{p,i}}{\sum_i y_i c_{v,i}} = \frac{y_{CO2}\frac{cp_{CO2}}{R} + y_{CH4}\frac{cp_{CH4}}{R}}{y_{CO2}\left(\frac{cp_{CO2}}{R} - 1\right) + y_{CH4}\left(\frac{cp_{CH4}}{R} - 1\right)} \tag{23}$$

The relationship $c_p - c_v = R$ is here exploited in the two terms of the denominator. Molar fraction for both CO2 and CH4 will obviously change in the two stages.

The model is ready to evaluate the compressor consumptions:

$$E = \frac{RT}{0.75} \frac{q}{22414} \frac{\gamma}{\gamma - 1} \left(\frac{p_{out}}{p_{in}}\right)^{\frac{\gamma - 1}{\gamma} - 1} \tag{24}$$

where:

0.75 is the isoentropic efficiency η_{is} of both compressors

22414 is the molar volume conversion factor $[\frac{cm^3}{mol}]$

p_{out} is the outlet pressure of the compressor

p_{in} is the inlet pressure of the compressor

Also this calculation will be repeated for the two stages.

Final output of the model are:

y_{p1} molar fraction of CO2 in the first permeate

q_{p1} total flow rate in the first permeate

x_{o1} molar fraction of CO2 in the first retentate

q_{o1} total flow rate in the first retentate

$A1$ area of the first membrane

y_p molar fraction of CO2 in the second permeate

q_p total flow rate in the second permeate

x_{o2} molar fraction of CO2 in the second retentate

q_{o2} total flow rate in the second retentate

$A2$ area of the second membrane

$E1$ electric consumption of the first compressor

$E2$ electric consumption of the second compressor

3.3.1 Model results for Matrimid

Quantities and parameters have been entered into our model as reported here:

$p_{feed} = 1\ bar$

$p_l = 1\ bar$ (minimum pressure permeate side)

$p_h = 100\ bar$ (maximum pressure feed side)

$P_{CO2} = 2.790\ barrer$

$P_{CH4} = 0.031\ barrer$

$q_f = 400\ m^3/h\ of\ biogas$ (this is a typical value for medium/small size biogas upgrading plant)

$x_f = 0.35$ (typical value of CO2 molar fraction in biogas streams)

$R = 0.9$ (minimum final recovery)

$R_1 = 0.95$ (first stage CO2 recovery)

$l = 80\ \mu m$

$T = 293.15\ K$

Results for Matrimid are here reported for two cases of $p_h = 100\ bar$ and $p_l = 50\ bar$:

pmax [bar]	Final CO2 fraction	Area 1 [m2]	Area 2 [m2]	E1 [W]	E2 [W]	CO2% in first retentate
100	89,88%	5,02*10^5	1,19*10^5	119,1 kW	58,39 kW	3,47%
50	87,61%	1,17*10^6	2,96*10^5	93,75 kW	48,94 kW	3,66%

Table 6.2: Model results for Matrimid membrane

Although this membrane seems to guarantee a relatively good separation of the two streams, both in 100 bar and 50 bar cases the final purity of CO2 is not high enough respect to an expected 96% of separation.

3.3.2. Alternative solutions

Results obtained for Matrimid membrane are now compared with other three possible solutions which are chosen from the **Robeson curve**. These diagrams express a tradeoff between permeability and selectivity which could be considered as general in polymeric membranes: with high permeability, and therefore able to dispose of high flows of gaseous mixture to be purified, membranes are characterized by low selectivity; conversely, membranes with high separation efficiency, i.e. able to purify the gas more, are usually less permeable.

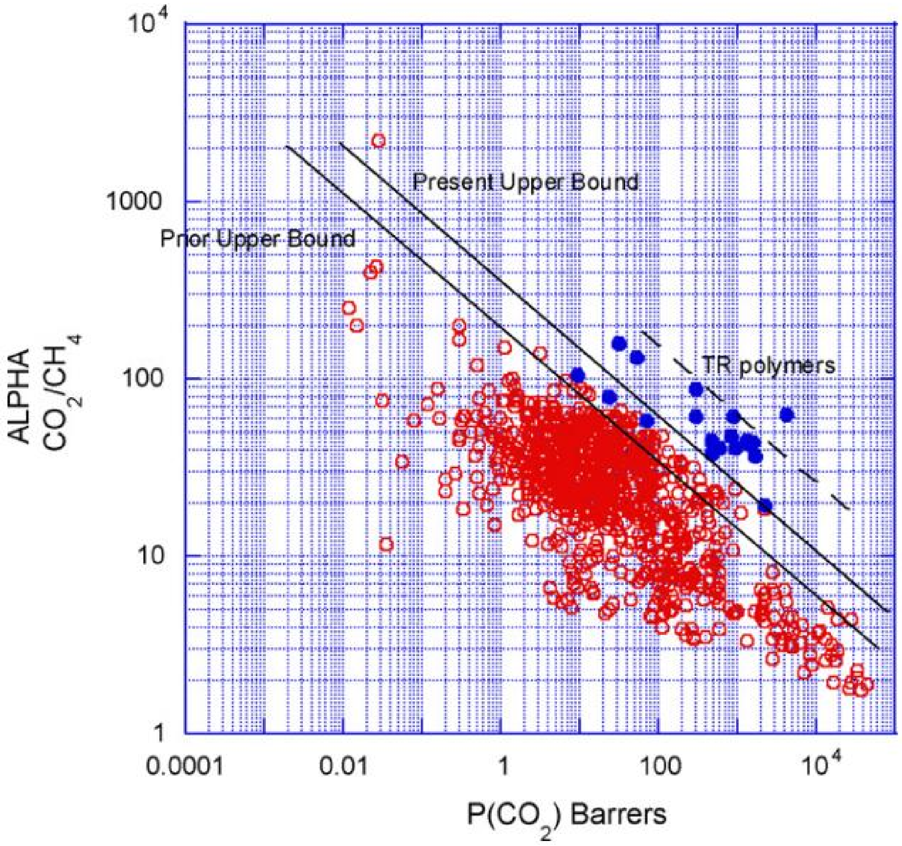
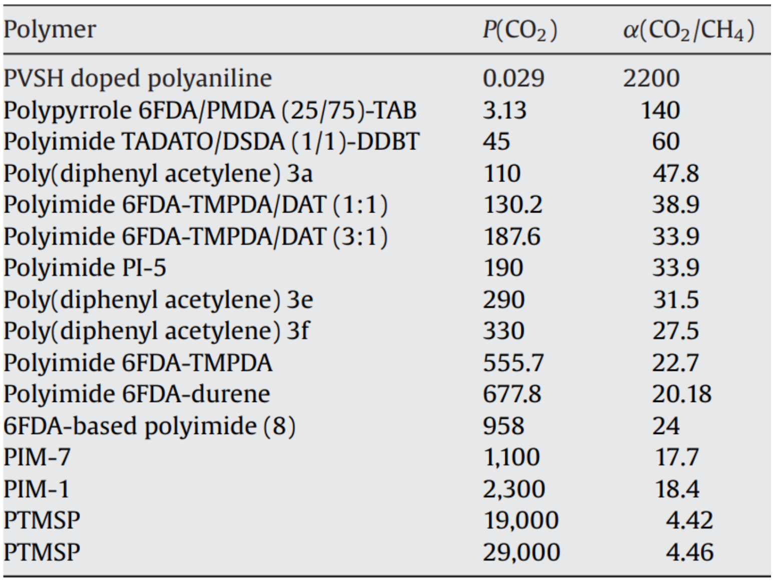


Figure 3.3: Upper bound correlation for CO2/CH4 separation

As illustrated in the figure, Robeson defined the so called 'upper bound' that is the limit in terms of maximum achievable value for permeability and selectivity for different pairs of gas, in this case CO2/CH4.
In the following table are present experimental data points close to the present empirical upper bound for CO2/CH4 separation.



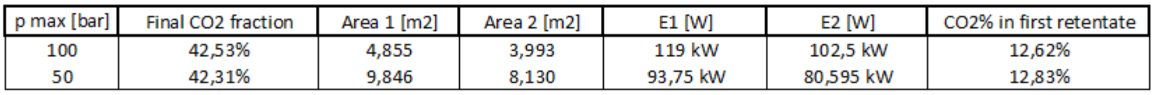
Polymer	$P(CO_2)$	$\alpha(CO_2/CH_4)$
PVSH doped polyaniline	0.029	2200
Polypyrrole 6FDA/PMDA (25/75)-TAB	3.13	140
Polyimide TADATO/DSDA (1/1)-DDBT	45	60
Poly(diphenyl acetylene) 3a	110	47.8
Polyimide 6FDA-TMPDA/DAT (1:1)	130.2	38.9
Polyimide 6FDA-TMPDA/DAT (3:1)	187.6	33.9
Polyimide PI-5	190	33.9
Poly(diphenyl acetylene) 3e	290	31.5
Poly(diphenyl acetylene) 3f	330	27.5
Polyimide 6FDA-TMPDA	555.7	22.7
Polyimide 6FDA-durene	677.8	20.18
6FDA-based polyimide (8)	958	24
PIM-7	1,100	17.7
PIM-1	2,300	18.4
PTMSP	19,000	4.42
PTMSP	29,000	4.46

Table 3.3: Permeability and selectivity for upper-bound polymeric membranes

The choice is to compare with our model the behavior of three different membranes, one in the upper part of the graph, one in the middle, one in the bottomed. This means comparing three different levels of permeability and selectivity:

1. **Poly(1-trimethylsilyl-1-propyne) (PTMSP),** high CO2 permeability and low CO2/CH4 selectivity

$$P_{CO2} = 29000\ barrer;\ \alpha = 4.46;\ t =\ 35\ \mu m$$

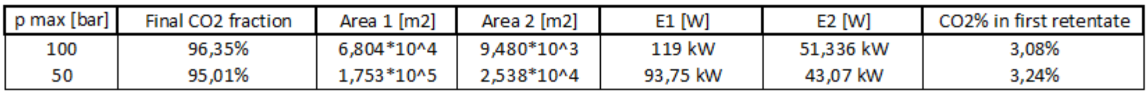


p max [bar]	Final CO2 fraction	Area 1 [m2]	Area 2 [m2]	E1 [W]	E2 [W]	CO2% in first retentate
100	42,53%	4,855	3,993	119 kW	102,5 kW	12,62%
50	42,31%	9,846	8,130	93,75 kW	80,595 kW	12,83%

Table 3.4: Model results for PTMSP membrane

2. **Polypyrrole 6FDA/PMDA (25/75)-TAB**, mid CO2 permeability and mid CO2/CH4 selectivity

$$P_{CO2} = 3.13\ barrer;\ \alpha = 140;\ t =\ 10\ \mu m$$



p max [bar]	Final CO2 fraction	Area 1 [m2]	Area 2 [m2]	E1 [W]	E2 [W]	CO2% in first retentate
100	96,35%	6,804*10^4	9,480*10^3	119 kW	51,336 kW	3,08%
50	95,01%	1,753*10^5	2,538*10^4	93,75 kW	43,07 kW	3,24%

Table 3.5: Model results for Polypyrrole 6FDA/PMDA (25/75)-TAB membrane

3. **PVSH doped polyaniline,** low CO2 permeability and high CO2/CH4 selectivity

$$P_{CO2} = 0.29\ barrer;\ \alpha = 2200;\ t = 10\ \mu m$$

p max [bar]	Final CO2 fraction	Area 1 [m2]	Area 2 [m2]	E1 [W]	E2 [W]	CO2% in first retentate
100	99,98%	1,008*10^7	2.440*10^5	119 kW	40,64kW	2,66%
50	99,95%	4,2395*10^7	6,836*10^5	93,75 kW	32,848 kW	2,70%

Table 3.6: Model results for PVSH doped polyaniline membrane

Comparison between results shows some evidences: membranes with high permeability are not useful for our model as our aim is to guarantee the highest possible separation trying to obtain a good compromise with costs and membrane area dimension.

PTMSP membrane is soon discarded as it has a too small percentage of separation. PVSH doped polyaniline membrane is the one with the highest molar fraction of permeated CO2, nevertheless the area of the first stage is almost two order of magnitude higher respect to the others, costs related to this option could be very high. The final comparison is between Matrimid and Polypyrrole 6FDA/PMDA (25/75)-TAB: the second one has higher a higher purity, lower membranes area, similar electrical consumptions and lower fraction of CO2 in the retentate (that means higher purity of CH4 that will be sent to grid).

The final choice is **Polypyrrole 6FDA/PMDA (25/75)-TAB**.

CHAPTER 4: WATER ELECTROLYSIS

In parallel to CO2 separation on MATLAB an alkaline electrolysis of water has been modelled on ASPEN environment in order to produce an H2 stream that will be mixed with CO2-rich flow.

Water electrolysis is a chemical process that uses an electric current to split water molecules into hydrogen (**H2**) and oxygen (**O2**) gas. The process takes place in an electrolytic cell, which contains two electrodes - a **cathode** and an **anode** - that are separated by a membrane or a diaphragm. Water is the electrolyte used in water electrolysis.

During water electrolysis, an external electric current is passed through the electrolytic cell, causing water molecules to split apart into their constituent ions - hydrogen ions (H+) and hydroxide ions (OH-). The hydrogen ions are attracted to the cathode, where they receive electrons and become hydrogen gas (H2), while the hydroxide ions are attracted to the anode, where they lose electrons and become oxygen gas (O2). The overall reaction is:

$$2H_2O \rightarrow 2H_{2(g)} + O_{2(g)} \tag{25}$$

Water electrolysis is a well-established technology for hydrogen production and is used in a variety of industrial applications, including the production of hydrogen for fuel cells, the manufacture of chemicals, and the production of high-purity metals. It is generally considered to be a more efficient and cost-effective method of hydrogen production than other methods, such as steam reforming of natural gas. However, it requires a significant amount of electricity, which can limit its use in some applications.

4.1. Fundaments of electrochemistry

In an electrochemical reaction, electrodes are responsible for the production of an electrical field which provoke chemical reactions. Usually, the electrodes are solid metals or semiconductors. In addition to the electrode, two types of electric charge conductors are required to form an external circuit (**electronic conductor**) and an internal circuit **(ionic species conductor**). The medium that is conductive to ionic species is denoted as **electrolyte**. Thenceforth, in electrochemistry, the electric energy is the driver that provides at least the free energy required for the desired reaction to occur.

The ionic species are exchanged between the two reactions through the medium of electrolyte, whereas the electrons are transferred through the external circuit. The negative electric charge that passes though the external circuit (electrons) must be equal to the positive electric charge of ionic specifies passing through the electrolyte.

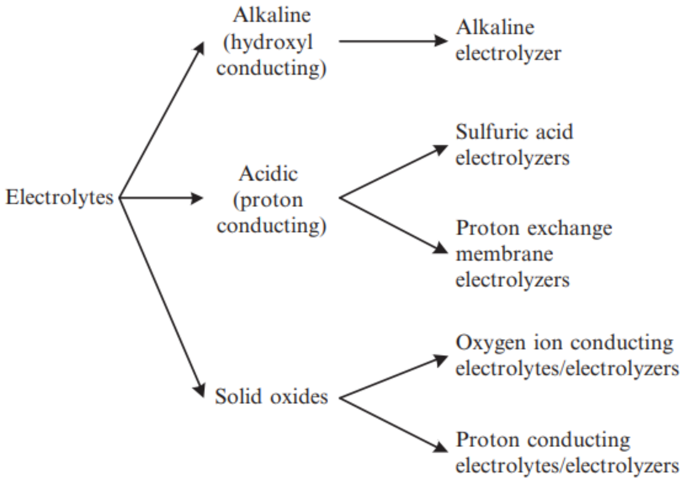


Figure 4.1: Electrolytes classification based on electrolyte type

Electrolysis process involves several principles from thermodynamics, kinetic, and transport phenomena.

Thermodynamic is concerned with the energy changes that occur during a chemical reaction. During electrolysis, the electrical energy provided to the system is used to drive a chemical reaction, and the thermodynamics of the reaction determines whether it is possible or not. The thermodynamic principles of electrolysis are governed by the Gibbs free energy change, which is related to the standard electrode potential of the cell.

Kinetics deals with the rate at which a chemical reaction occurs. During electrolysis, the rate of the chemical reaction depends on the applied potential difference, concentration of the electrolyte, and the nature of the electrodes. The kinetics of the electrode reactions can be described using the Butler-Volmer equation, which relates the rate of the reaction to the overpotential (the difference between the applied potential and the equilibrium potential) and the concentration of the electrolyte.

Transport phenomena deals with the movement of charged particles (ions) and neutral particles in a fluid medium. During electrolysis, the charged particles (ions) move towards the electrodes under the influence of the applied potential difference. This movement of ions is described by the Nernst-Planck equation, which relates the flux of ions to the concentration gradient and the electric field. The neutral particles, on the other hand, move under the influence of diffusion, which is described by Fick's laws of diffusion.

In summary, electrolysis involves several principles from thermodynamics, kinetics, and transport phenomena, which are used to understand and optimize the process.

4.2. Alkaline electrolysis

As its name suggests, alkaline electrolyzers (AE) use an alkaline electrolyte (pH>7).

In an alkaline electrolyte, the mobile ionic species are anions (negative ions) of the hydroxyl group, OH^-. The electrochemical half-cell reactions in an alkaline electrolyzer cell are as follow:

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \text{ at cathode} \tag{26}$$

$$2OH^- \rightarrow H_2O + 0.5O_2(g) + 2e^- \text{ at anode} \tag{27}$$

Water is supplied at the cathode, which is made of inexpensive materials such as stainless steel coated with nickel. The anolyte solution—here water-generated must be recirculated to reduce the concentration of overpotentials. The anode material is typically nickel. The anolyte passes through an electrolyte separator above which oxygen gas evolves.

The process of alkaline electrolysis involves the following steps:

1. Electrolyte Preparation: A concentrated solution of KOH or NaOH is prepared and used as the electrolyte. The concentration of the electrolyte solution can vary depending on the desired current density and temperature.
2. Electrolysis Cell: The electrolysis cell consists of two electrodes, an anode and a cathode, separated by a membrane. The anode is typically made of a metal such as nickel or titanium, while the cathode is made of a porous material such as nickel foam.
3. Electrolysis Process: When a voltage is applied across the electrodes, water molecules (H2O) at the cathode are reduced to hydrogen gas (H2) and hydroxide ions (OH-). At the anode, water molecules are oxidized to oxygen gas (O2) and hydrogen ions (H+). The hydrogen ions combine with the hydroxide ions in the electrolyte to form more water molecules, completing the cycle.
4. Gas Separation: The hydrogen and oxygen gases produced during electrolysis are separated by a gas separator, typically a pressure swing adsorption (PSA) unit or a membrane separator.
5. Gas Compression and Storage: The hydrogen gas produced during electrolysis is typically compressed and stored for use as a fuel, while the oxygen gas is usually vented to the atmosphere.

Alkaline electrolysis is commonly used in the production of hydrogen for fuel cells and other industrial processes. It is a mature technology and has been used commercially for several decades.

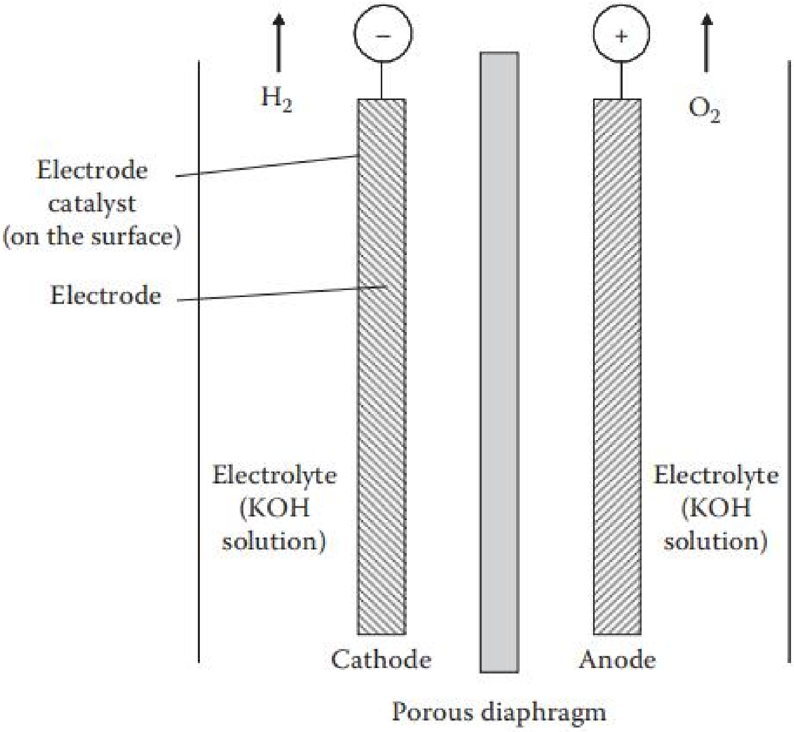


Figure 4.2: Generic scheme of an alkaline electrolyzer

Alkaline electrolytes are commonly used in batteries and other electrochemical systems, in addition they show several properties that make them desirable for these types of applications. These include as first high conductivity as they have high ionic conductivity, which means that they can facilitate the movement of charged particles (ions) through the electrolyte solution. This property is important for efficient electrochemical reactions. In particular the efficiency of alkaline electrolysis is typically in the range of 60-80%, depending on the operating conditions and the efficiency of the electrolysis cell.

For sure a key point is the stability as these types of electrolytes can withstand a wide range of operating conditions without breaking down or reacting with other materials in the system. This makes them a reliable choice for long-term use.

They have generally a low cost, alkaline electrolytes are often less expensive than other types of electrolytes, making them a cost-effective choice for many applications.

Moreover, environmental alkaline electrolytes are generally considered to be environmentally friendly because they do not contain toxic or hazardous materials.

4.2.1. Electrical overpotential

Electrical overpotential in alkaline electrolyzers is the additional voltage required to drive the electrolysis reaction beyond the thermodynamic potential due to the activation energy required for the reaction to occur. In other words, it is the voltage required to overcome the resistance of the electrolyte and the electrode surfaces and to initiate the electrolysis process.

The electrical overpotential in alkaline electrolyzers can be influenced by a variety of factors, such as the type and concentration of the electrolyte, the electrode material, the operating temperature, and the flow rate of the electrolyte. The overpotential is typically highest at the beginning of the electrolysis process, when the electrolyte and electrode surfaces are not yet fully activated and decreases as the reaction progresses.

Reducing the electrical overpotential is important for improving the energy efficiency and overall performance of alkaline electrolyzers. This can be achieved through a variety of strategies, such as optimizing the electrode materials and surface properties, selecting appropriate operating conditions, and improving the design of the electrolysis cell.

One approach to reducing the electrical overpotential is to use more efficient electrode materials, such as platinum, which have lower activation energies and can operate at lower overpotentials. Another approach is to increase the operating temperature, which can decrease the resistance of the electrolyte and improve the electrode activation.

Overall, minimizing electrical overpotential is an important consideration in the design and operation of alkaline electrolyzers, as it can significantly impact the efficiency and performance of the electrolysis process.

4.2.2. Configurations

There are two main types of alkaline electrolyzers: monopolar and bipolar.

In a monopolar configuration electrolysis cells are in series, the voltage applied to the cell is the sum of voltages for each cell while the current that flows is the same:

$$E_{AE} = \sum E_{cell} = (N_{cell} - 1)E_{cell} \tag{28}$$

Monopolar alkaline electrolyzers have a single electrode chamber, where both the anode and cathode are located. The electrolyte solution flows through this chamber and is split into hydrogen and oxygen gas at the two electrodes. Monopolar electrolyzers are generally less efficient than bipolar electrolyzers, because they suffer from significant ohmic losses due to the large distance between the electrodes.

In a bipolar configuration the cells are connected in parallel such that the voltage is the same for all cells, while the total current is given as follows:

$$I_{AE} = \sum I_{cell} = N_{cell} I_{cell} \tag{29}$$

Bipolar alkaline electrolyzers, on the other hand, have multiple electrode chambers, with each chamber containing both an anode and a cathode. The chambers are separated by a bipolar plate, which conducts electricity between adjacent electrode chambers. The electrolyte solution flows through the chambers and is split into hydrogen and oxygen gas at the two electrodes. Bipolar electrolyzers are more efficient than monopolar electrolyzers, because they have a shorter distance between the electrodes, which reduces electrical losses.

4.3. Electrolyzer ASPEN model

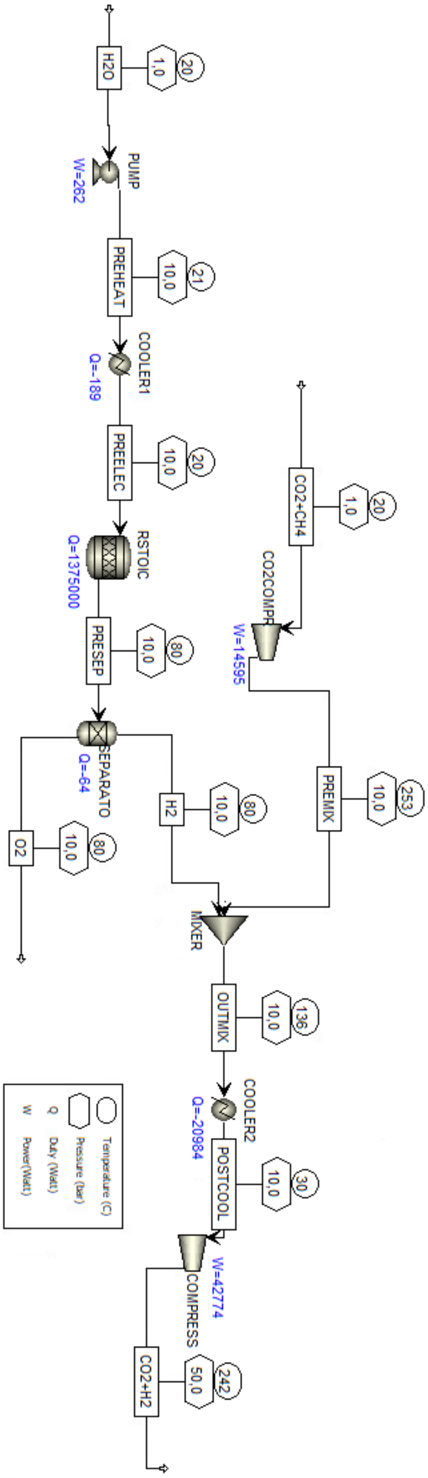


Figure 4.3: ASPEN model of the electrolyzer

In figure 3.3. the ASPEN model of the electrolyzer is shown. The two streams of CO2+CH4 and H2O enter in parallel.

The CO2-rich stream presents values and properties obtained from the previous model in MATLAB: CO2 molar composition is 96.35%, CH4 represents only the 3.65%. The temperature is 20°C and the pressure is 1 bar. The total stream is the one obtained from the two stages of permeation and that is 132.94 cm^3/h. The stream is sent to a compressor that comprises until 10 bar which is the pressure of the next block, the mixer. It is assumed an isentropic efficiency of compression $\eta_{is} = 0.75$ (this value will be the same for all the compression in this model and in the reactor block) while mechanical efficiency is 100%. The electrical consumption is 14.595 kW and the outlet temperature is 253°C (200.164°C is the isentropic outlet temperature).

On the other side flows a water stream at 20°C and 1 bar, the total rate is evaluated from the stoichiometric balance and on the assumption that the **H2/CO2 ratio** is equal to 3. This ratio is important because it affects the quality and quantity of the products that are produced in certain chemical reactions. Specifically, it is important in reactions involving the conversion of carbon dioxide (CO2) and hydrogen (H2) into other chemicals, such as methane (CH4) and other hydrocarbons as methanol in this case. For example, when the H2/CO2 ratio is high (more H2 than CO2), the reaction tends to favor the production of methane and water. On the other hand, when the H2/CO2 ratio is low (more CO2 than H2), the reaction tends to favor the production of carbon monoxide and higher hydrocarbons. For our scope the evaluation of the water flow rate is related to the evaluation of H2 flowrate correspondent to the correct H2/CO2 ratio but this, in turn, is related to CO2-only stream:

$$q_{H2} = q_{H2O} * \frac{H2}{CO2} ratio = 0.9635 * 5.931 \frac{kmol_{CO2+CH4}}{h} * 3 = 17.143 \frac{kmol_{H2}}{h}$$

Water and hydrogen are in a stoichiometric relationship of 1:1 so at the end of the story:

$$q_{H2O} = q_{H2} = 17.143 \frac{kmol_{H2O}}{h}$$

This flow is then pumped to 10 bar with an electrical apport of 261.58 W and subsequently it is cooled to 20°C.

This flow now is ready to enter the effective block of electrolysis which is represented by a block called *RSTOIC* with a successive *Separator*.

The RSTOIC is a reactor type block used in ASPEN in which the reaction of water-splitting happens under the assumption of fractional conversion of water equal to 1 that means all of the water that is fed reacts to produce byproducts hydrogen and oxygen.

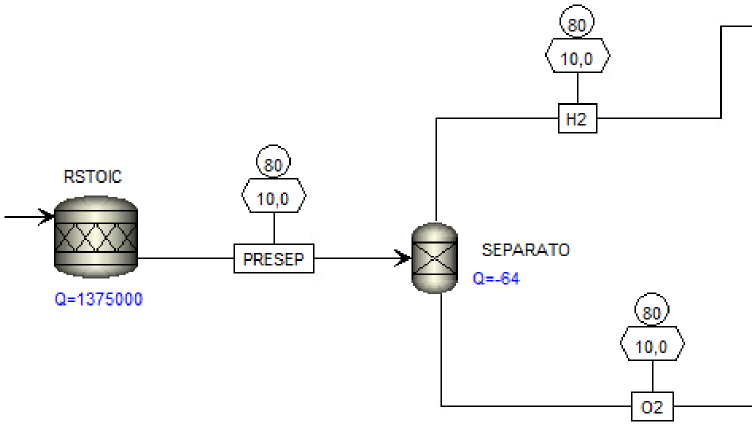


Figure 7.4: Electrolyzer block on ASPEN (RSTOIC + SEP)

The reactor operates at 80°C hypothesizing no pressure drops along the process. The heat duty is 1.375 MW.

The outgoing flow is sent to the separator block which splits an H2 stream of 17.143 $kmol/h$ while the oxygen stream is 8.5715 $kmol/h$.

The two streams finally meet in the mixer block at 10 bar pressure. The outgoing flow is as first cooled until 30°C and then compressed directly to 50 bar which is the pressure of the subsequent catalytic reactor. Heat duty of the cooler is -20,984 kW while the compressor requires a net work of 42.774 kW.

CHAPTER 5: METHANOL PRODUCTION

5.1. CO2 hydrogenation

CO2 hydrogenation is a chemical reaction that converts carbon dioxide (CO2) into useful chemicals, such as methanol (CH3OH) and formic acid (HCOOH), using hydrogen (H2) as a reducing agent. This reaction is a promising approach for reducing greenhouse gas emissions and producing valuable products from waste CO2.

The reaction typically occurs in the presence of a catalyst, such as copper, nickel, or iron-based catalysts. The general equation for the reaction is:

$$CO_2 + H_2 \rightarrow CH3OH \text{ or } HCOOH \tag{30}$$

The process can be performed under mild conditions, typically at temperatures ranging from 150 to 300°C and pressures ranging from 10 to 50 bar. The reaction rate and selectivity can be influenced by various factors, such as the catalyst type, the reaction temperature, and the H2/CO2 ratio.

The CO2 hydrogenation process can be coupled with the production of H2 from renewable sources, such as solar, wind, or hydro power, to create a closed carbon cycle that can reduce greenhouse gas emissions. This approach is known as the Power-to-X concept, where the excess renewable electricity is used to generate H2, which is then used to convert CO2 into useful chemicals.

In summary, CO2 hydrogenation by H2 is a promising approach for reducing greenhouse gas emissions and producing valuable chemicals. Ongoing research is focused on improving the efficiency and selectivity of this process, as well as developing new catalysts that can enhance the reaction rate and selectivity.

5.2. Catalytic reactors

Catalytic reactors are chemical reactors that use a catalyst to speed up a chemical reaction. The catalyst provides an alternative pathway for the reaction to occur, which lowers the activation energy required for the reaction to proceed. This results in faster reaction rates and often allows the reaction to occur at lower temperatures and/or pressures than would be required without the catalyst.

There are various types of catalytic reactors, including fixed-bed reactors, fluidized-bed reactors, and membrane reactors. In a fixed-bed reactor, the catalyst is typically placed in a bed, and the reactants are passed over the catalyst. The fluidized-bed reactor uses a fluid, such as gas or liquid, to suspend the catalyst particles, which results in better mixing and heat transfer. The membrane reactor integrates a catalyst with a permeable membrane, which allows for selective separation of products and reactants.

Catalytic reactors are used in many industries, including petrochemicals, fine chemicals, and pharmaceuticals. For example, in the petrochemical industry, catalytic reactors are used to convert crude oil and natural gas into various chemicals, such as ethylene and propylene. In the fine chemicals industry, catalytic reactors are used to produce high-value products, such as pharmaceuticals and agrochemicals.

The design and operation of catalytic reactors are critical for achieving high reaction rates and high product yields. The selection of catalyst, reactor type, and operating conditions depends on the specific reaction and desired product.

5.2.1. Chemical parameters

Selectivity, conversion, and yield are important parameters that are used to characterize the efficiency of a chemical reaction.

Selectivity refers to the percentage of reactants that are converted into a specific product in a chemical reaction. It is calculated by dividing the amount of the desired product by the total amount of all products formed.

$$S_p = \frac{\dot{n}_{p,\mathrm{out}} - \dot{n}_{p,\mathrm{in}}}{\dot{n}_{k,\mathrm{in}} - \dot{n}_{k,\mathrm{out}}} \left| \frac{\mu_k}{\nu_p} \right| \tag{31}$$

with n_p the moles of product p (in the inlet and outlet);
n_k is the limiting reagent k
μ_k and ν_p are the stoichiometric coefficients

Conversion is the percentage of the starting material that is converted into products in a chemical reaction. It is calculated by dividing the difference between the initial and final amounts of the starting material by the initial amount of the starting material.

$$X_i = \frac{\dot{n}_{i,in} - \dot{n}_{i,out}}{\dot{n}_{i,in}} = 1 - \frac{\dot{n}_{i,out}}{\dot{n}_{i,in}} \tag{32}$$

with $\dot{n}_i$ as the change of moles with time of species i.

Yield is the amount of product formed in a chemical reaction compared to the theoretical maximum amount of product that could be formed. It is calculated by dividing the actual amount of product obtained by the theoretical maximum amount of product that could be obtained, and multiplying by 100%.

High selectivity, high conversion, and high yield are desirable in most chemical reactions because they result in a more efficient use of resources and higher production of the desired product. However, achieving high selectivity, conversion, and yield can be challenging, as they are often influenced by a variety of factors, such as reaction conditions, catalyst type, and reactant concentrations.

At the end of the story, selectivity, conversion, and yield are important parameters used to evaluate the efficiency of a chemical reaction. By carefully controlling the reaction conditions and optimizing the choice of catalyst and reactant concentrations, it is possible to maximize selectivity, conversion, and yield and improve the overall efficiency of a chemical reaction and this is what will be done in the final part of the comparison of the results.

5.2.2. Plug Flow Reactor (PFR)

A Plug Flow Reactor (PFR) is a type of continuous flow reactor that is commonly used for the production of methanol. In a PFR the reactants are continuously fed into the reactor and the products are continuously removed, resulting in a steady-state flow of reactants and products through the reactor.

The PFR consists of a long tubular reactor, typically made of stainless steel, with a narrow diameter. The reactants are fed into one end of the reactor, and the catalyst is packed along the length of the reactor. As the reactants flow through the reactor, they react with the catalyst to produce methanol.

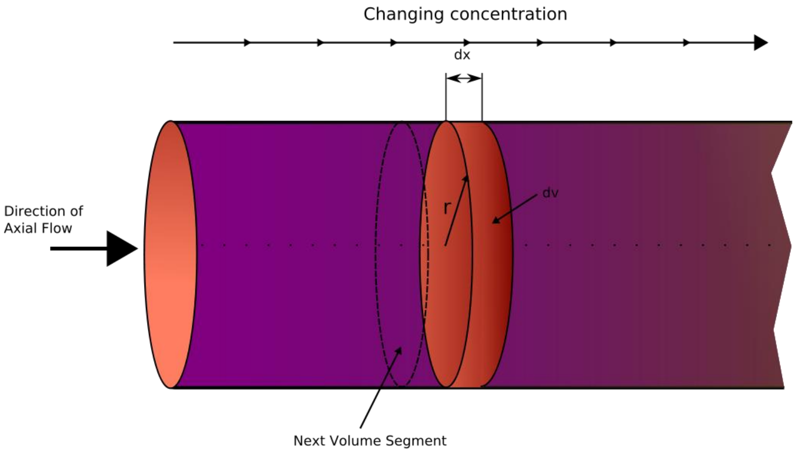


Figure 5.1: Simple scheme of a PFR

The PFR offers several advantages for the production of methanol, including high conversion rates, efficient use of the catalyst, and easy control of reaction conditions. The narrow diameter of the reactor ensures that the reactants and catalyst are in close contact, maximizing the efficiency of the reaction. Additionally, the steady-state flow of reactants and products through the reactor allows for precise control of reaction conditions, such as temperature and pressure.

However, the PFR also has some limitations, such as potential issues with catalyst deactivation and difficulties with catalyst loading and unloading. Additionally, the PFR requires precise control of reaction conditions to maintain a steady-state flow of reactants and products, which can be challenging in large-scale production. Overall, the PFR is a widely used reactor type to produce methanol due to its high efficiency and easy control of reaction conditions. Ongoing research is focused on improving the catalyst performance and developing new reactor designs to overcome some of the limitations of the PFR.

5.2.2.1. Thermodynamic and parameters of PFR

PFR behavior is influenced by a thermodynamics variables and other operative parameters.

As first temperature of the reactants and products is an important parameter in a PFR because it affects the reaction rate and selectivity. In general, higher temperatures lead to faster reaction rates, but may also decrease the selectivity and cause unwanted side reactions.

The pressure inside the PFR can also affect the reaction rate and selectivity. Higher pressures can increase the rate of reaction but may also require more energy to maintain the pressure and can lead to safety concerns.

Beyond the thermodynamic ones there are other operative parameters affecting the reactor behavior. As first the concentrations of the reactants in the feed stream can affect the reaction rate and selectivity. Higher concentrations of reactants can lead to faster reaction rates but may also cause unwanted side reactions and reduce selectivity.

The choice of catalyst and its concentration can have a significant impact on the reaction rate and selectivity in a PFR. The catalyst should be chosen based on its activity, selectivity, stability, and cost.

The flow rate of reactants and products is an important parameter in a PFR because it affects the residence time and the amount of time that the reactants have to react with the catalyst. Higher flow rates can lead to shorter residence times and faster reaction rates, but may also decrease the selectivity.

The length and diameter of the PFR are important parameters that determine the residence time and the amount of catalyst that is required. Longer reactors and smaller diameters can lead to longer residence times and higher reaction rates but may also increase the pressure drop and require more energy to maintain the flow.

5.3. Reaction kinetics

The velocity of the reaction is the specific rate of generated matter. It could be expressed in terms of mass or molar flow with respect a reference basis.

$$r = \frac{mass\ flowrate}{reference\ basis} \text{ or } R = \frac{molar\ flowrate}{reference\ basis}$$

Basis choice depends on the system properties:

for homogeneous reactions of fluid phases, it is considered the volume phase, so velocity is measured in $\left[\frac{kg}{s\,m^3}\right]$ or $\left[\frac{kmol}{s\,m^3}\right]$;

for solid-fluid heterogeneous reactions it is taken the active solid surface, so the rate becomes $\left[\frac{kg}{s\,m^2}\right]$ or $\left[\frac{kmol}{s\,m^2}\right]$;

the third case is for catalytic heterogenous reactions the catalyst mass is used so r and R are measured in in $\left[\frac{kg}{s\ kg_{cat}}\right]$ or $\left[\frac{kmol}{s\ kg_{cat}}\right]$;

Kinetic equations refers to the study of the rate at which chemical reactions occur, as well as the factors that influence reaction rates. This includes the examination of reaction mechanisms, reaction pathways, and the various steps involved in each reaction.

We consider a general reaction that transforms reactants A and B into products P and Q:

$A + B \rightarrow P + Q$ (with kynetics constant k_1) and its reverse $P + Q \rightarrow A + B$ (with kynetics constant k_2).

The reaction rate of the process is expressible as a function of the composition and physical conditions of the system by means of a relationship whose foundations reside in the so-called law of mass action:

$$R_A = -k1\ C_A^a C_B^b + k2\ C_P^p C_Q^q \tag{33}$$

where:
$k1$ and $k2$ are the kinetics constant of the process
a, b, p, q are reaction orders with respect different components

This is an example of kinetic equation. It can assume a simplifies form if the reverse transformation reaction of the products P and Q in reactants A and B is extremely slow compared to the direct reaction. In this case, the process is called irreversible and in terms of the relative values of the constants kinetics, it can be stated that k_1 >>> k_2. So in this case the equation becomes $R_A = -k_1 C_A^a C_B^b$.

For the case of only one reagent A with $a = 1$ the kinetics is called linear and becomes $R_A = -k_1 C_A$.
For processes with a complex reaction scheme, the kinetic model consists of a system of several equations, which expresses the rates of generation of matter of the various species.

Temperature has a significant effect in this type of equations. Generally, increasing the temperature of a reaction will increase the rate of the reaction, while decreasing the temperature will slow it down. This is due to the fact that increasing temperature increases the kinetic energy of the molecules, which allows them to overcome the activation energy barrier required for the reaction to occur.

The relationship between temperature and reaction rate is described by the Arrhenius equation, which states that the rate constant of a reaction increases exponentially with increasing temperature. Specifically, the equation is:

$$k = A\, e^{\left(-\frac{Ea}{RT}\right)} \tag{34}$$

where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the absolute temperature.

As reported in the graph below, the activation energy plays a key role whit increasing T.

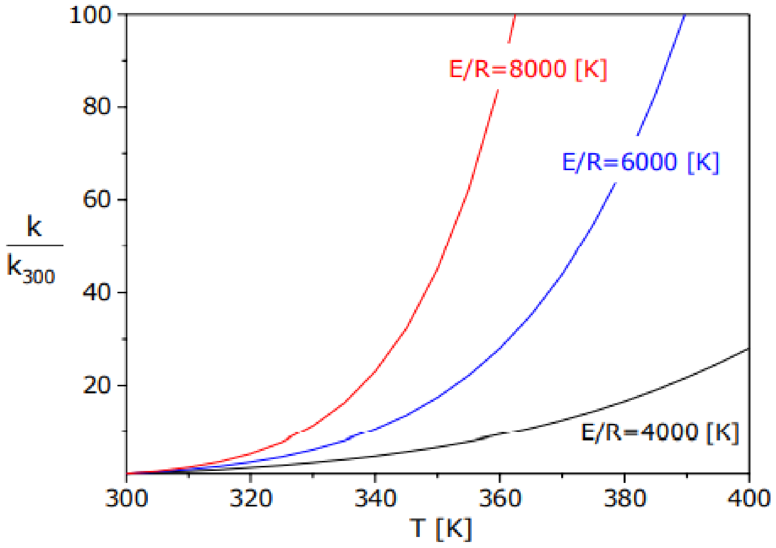


Figure 5.2: Relationship T vs k/k300

When the reaction is reversible the activation energies to be taken into account are two, here in the graph below it is highlighted the temperature effect on the rate (velocity):

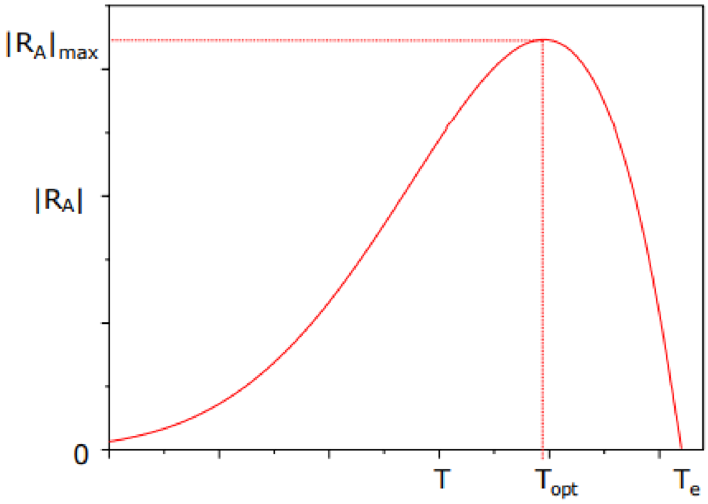


Figure 5.3: Absolute temperate on the reaction velocity

On the graph T_{opt} is the temperature correspondent to the optimal productive condition in which the reaction has the highest velocity.

Reaction kinetics is important in a wide range of fields, including chemistry, biochemistry, and materials science. Understanding the kinetics of a reaction can help scientists design more efficient processes and develop new materials.

Some of the factors that can influence reaction kinetics include temperature, concentration, pressure, and the presence of catalysts or inhibitors. By manipulating these factors, scientists can often control the rate at which a reaction occurs, which can be useful in many different applications.

5.3.1. Water-gas shift

The water gas shift reaction is an important industrial process that is used to produce hydrogen and carbon dioxide from a mixture of carbon monoxide and steam. The reaction is often used in the production of synthesis gas (syngas), which is a mixture of carbon monoxide and hydrogen that can be used as a feedstock to produce chemicals and fuels.

The chemical equation for the water gas shift reaction is:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{35}$$

In this reaction, carbon monoxide reacts with water to form carbon dioxide and hydrogen. The reaction is exothermic and typically occurs at temperatures between 200-300°C.

The water gas shift reaction is often used in conjunction with other processes, such as steam reforming of natural gas, to produce hydrogen for fuel cell applications. The reaction can also be used to remove carbon monoxide from industrial gas streams, such as

More related to our work, the **reversed water gas shift reaction** is the reverse of the water gas shift reaction and involves the conversion of carbon dioxide and hydrogen into carbon monoxide and water as it follows:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{36}$$

This reaction is endothermic and typically occurs at temperatures above 200°C. The reaction can be catalyzed by a variety of materials, including transition metal oxides and noble metal catalysts.

The reversed water gas shift reaction is important for a number of applications, including the production of syngas, the removal of carbon dioxide from industrial gas streams, and the production of carbon monoxide for chemical synthesis. In some cases, the reaction may be used in conjunction with the water gas shift reaction to adjust the ratio of carbon monoxide and hydrogen in a gas stream.

The reversed water gas shift reaction is also being studied as a potential means of converting carbon dioxide into useful chemicals and fuels, as well as a potential means of storing renewable energy. For example, excess electricity generated from renewable sources can be used to produce hydrogen, which can then be converted into carbon monoxide via the reversed water gas shift reaction. The resulting carbon monoxide can be used as a feedstock for the production of chemicals or fuels, or it can be stored and later used to generate electricity via fuel cells.

5.3.2. Methanol kinetics

To correctly define methanol kinetics on ASPEN Plus, the rate constant and equilibrium constant must be defined properly. For this reason for the reaction rate constant the basis is $kmol/(kg_{cat}\ s\ Pa)$ for an overall first-order reaction in terms of reacting species.

In the model two main reactions will be considered. The first one is methanol production from carbon dioxide and hydrogen:

$$CO_2 + 3H_2 \leftrightarrow CH3OH + H_2O \tag{37}$$

the kinetic constant is defined as follows in the Eq.(38):

$$r_{\mathrm{CH_3OH}}(\mathrm{kmol/kg\,cat \cdot s}) = \frac{\left(1.07\times10^{-13}\times e^{(4{,}413.76/T)}\times P_{\mathrm{CO_2}}\times P_{\mathrm{H_2}} - 4.182\times10^{7}\times e^{(-2{,}645.966/T)}\times\frac{P_{\mathrm{CH_3OH}}\times P_{\mathrm{H_2O}}}{P_{\mathrm{H}}^{2}}\right)}{(1+3{,}453.38\times(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})+1.578\times10^{-3}\times e^{(2{,}068.44/T)}\times P_{\mathrm{H_2}}^{0.5}+6.62\times10^{-16}\times e^{(14{,}928.915/T)}P_{\mathrm{H_2O}})^{3}}$$

The second reaction is the reversed water-gas shift:

$$\mathrm{CO2 + H2 \leftrightarrow CO + H2O} \tag{39}$$

with kynetic constant defined in Eq.(40):

$$r_{\mathrm{CO}}(\mathrm{kmol/kg\,cat \cdot s}) = \frac{\left(122\times e^{(-(11{,}398.24/T))}\times P_{\mathrm{CO_2}} - 1.1412\times e^{(-(6624.98/T))}\times\frac{P_{\mathrm{CO}}\times P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}}\right)}{(1+3453.4\times(P_{\mathrm{H_2O}}/P_{\mathrm{H_2}})+1.578\times10^{-3}\times e^{(2068.4/T)}\times P_{\mathrm{H_2}}^{0.5}+6.62\times10^{-16}\times e^{(14{,}928.9/T)}P_{\mathrm{H_2O}})^{1}}$$

These equations are in the Langmuir-Hinshelwood–Hougen–Watson (**LHHW**) form and are classified as non-conventional kinetics type reaction. These equations highlight the contribution of three main effects:

Kinetics: The LHHW equation assumes a particular form for the rate law of the reaction, which is often based on experimental data. The kinetics of the reaction can influence the rate constant and the reaction orders used in the LHHW equation. For example, the power law kinetics form assumes that the reaction rate is proportional to the concentration of the reactants raised to a power, while the Langmuir-Hinshelwood kinetics form assumes that the reaction rate is proportional to the product of the surface coverage of the reactants. Thus, the choice of kinetics form can affect the LHHW equation.

Adsorption: Many chemical reactions occur at the surface of a catalyst, and adsorption of the reactants onto the surface can affect the reaction rate. The Langmuir-Hinshelwood kinetics form explicitly accounts for adsorption effects by including Langmuir adsorption constants for the reactants. The adsorption process can influence the surface coverage of the reactants and the availability of active sites on the surface, which can affect the reaction rate.

Driving force: The driving force for a chemical reaction is the difference between the free energy of the reactants and the free energy of the products. The LHHW equation assumes that the reaction rate is proportional to the driving force for the reaction. Thus, changes in the free energy of the reactants or products can affect the reaction rate and the LHHW equation. For example, changes in temperature, pressure, or the concentration of the reactants can alter the driving force and affect the reaction rate.

Considering these three contributions the general expression for LHHW equation is:

$$r = \frac{(kinetic\ factor)(driving\ force\ expression)}{(adsorption\ term)} \tag{41}$$

5.4. Separation columns

Separation columns are an essential component of many chemical processes, particularly in the petroleum, chemical, and pharmaceutical industries. They are used to separate components of a mixture based on their physical and chemical properties, such as boiling point, molecular weight, and polarity.

A separation column typically consists of a vertical column packed with a material that allows for the separation of the components in the mixture. The column is typically filled with a packing material, such as structured packing, random packing, or trays, which provides a large surface area for contact between the vapor and liquid phases of the mixture

The mixture is introduced into the column, and a heat source is applied to the bottom of the column to vaporize the mixture. As the vapors rise up the column, they come into contact with the packing material, which causes them to condense and re-vaporize multiple times. This process allows the different components of the mixture to separate based on their physical and chemical properties.

The separated components are then collected at different points along the column, depending on their boiling points and other properties. The efficiency of the separation depends on factors such as the packing material used, the operating conditions, and the composition of the mixture.

5.4.1. Distillation columns

The most common type of column of separation is a distillation column, which is used to separate a mixture of two or more liquids based on their boiling points. Distillation is a separation process that relies on the differences in boiling points of the components in a mixture.

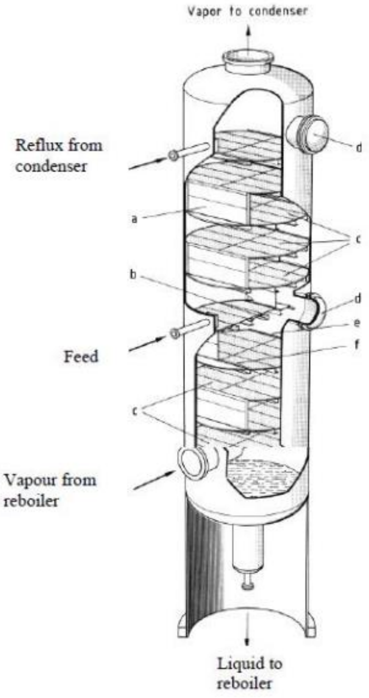


Figure 5.4: Representation of a distillation column

A distillation column consists of a vertical tower that is packed with a column packing material, such as trays or structured packing. The mixture to be separated is fed into the column from the bottom, and a heat source is applied at the bottom of the column. As the mixture is heated, the components with lower boiling points will vaporize and rise up the column, while the components with higher boiling points will remain in the liquid phase and flow down the column.

The rising vapor is partially condensed as it travels up the column, and the condensate flows down the column as a liquid, called the reflux. The reflux helps to improve the separation by allowing the more volatile components to vaporize and be carried up the column. The condensed vapor is collected at the top of the column and the liquid reflux is collected at the bottom of the column.

The separation in a distillation column depends on several factors, including the boiling points of the components, the temperature and pressure of the column, the composition of the feed mixture, and the design of the column. The efficiency of the separation can be improved by increasing the number of trays or the height of the column.

5.4.1.1. Components

Summing up the main components of a distillation column include:

The column shell is a tall, cylindrical vessel that houses the internal components of the column. It is typically made of metal, such as stainless steel or carbon steel, and can be insulated to minimize heat losses.

Column packing is the material inside the column that provides a large surface area for the separation of the mixture. There are various types of packing materials, such as trays or structured packing. The choice of packing material depends on the specific application, the composition of the mixture, and the desired separation efficiency.

The reboiler is a heat exchanger located at the bottom of the column that heats the liquid mixture to its boiling point. The heat source can be steam, hot oil, or electric heaters. The vapor generated by the reboiler provides the driving force for the separation process.

The condenser is located at the top of the column and is responsible for cooling the vapor that rises the column. The condensed vapor is collected as a liquid product, which is separated from the remaining vapor.

The reflux drum is a vessel located at the top of the column that collects the condensed vapor and the liquid reflux. The reflux is returned to the column to improve the separation efficiency by providing additional contact between the vapor and the liquid.

Trays are horizontal plates or decks that are placed inside the column and provide a surface for the separation of the mixture. The trays are typically perforated or have holes that allow vapor to flow through while holding back the liquid. The trays can be designed to provide more or less contact between the vapor and the liquid, depending on the specific separation requirements.

5.4.2. Flash separation

Flash separation is a process used in chemical engineering to separate components of a mixture based on their volatility. It is a type of distillation that involves the rapid vaporization of a liquid mixture followed by the immediate condensation of the vapors to separate the more volatile components from the less volatile ones.

In a flash separation process, a liquid mixture is heated to a high temperature and then rapidly depressurized. This causes the more volatile components of the mixture to vaporize and separate from the less volatile ones. The vapors are then condensed and collected, while the remaining liquid mixture is processed further to remove any remaining volatile components.

Flash separation is commonly used in the petroleum industry to separate crude oil into different fractions, such as gasoline, diesel fuel, and kerosene. It is also used in the production of chemicals and pharmaceuticals to separate and purify different components of a mixture.

5.4.2.1. Components

The basic components of a flash separator include:

Inlet nozzle, where the mixture to be separated is introduced into the vessel. Vessel is the main body of the separator where the separation takes place. It is typically cylindrical or spherical in shape and is designed to withstand high temperatures and pressures.

Flash valve is a valve located at the bottom of the vessel that is used to release the separated vapor from the separator. The valve is designed to maintain a constant pressure in the separator.

Condenser is a heat exchanger located outside the vessel that is used to condense the separated vapor back into a liquid form.

Liquid outlet is an outlet located at the bottom of the separator where the separated liquid is removed from the vessel while vapor outlet is an outlet located at the top of the separator where the separated vapor is removed from the vessel.

Control systems: level control system is used to maintain the liquid level within the separator. Heating system is used to heat the mixture to a temperature where separation can occur. Pressure control system maintains the pressure within the separator at a constant level.

5.5. Recycle section

A recycle section is commonly used in chemical reactors to improve the efficiency and productivity of the process. It involves returning a portion of the product stream back to the reactor after it has been separated from the desired product.

There are several reasons why a recycle section may be used in a reactor block, including for sure an increasing in reaction yield, in fact by recycling unreacted starting materials or byproducts back into the reactor, the reaction can be driven towards completion, resulting in a higher yield of the desired product.

Also selectivity can be enhanced by recycling a specific product or intermediate in order to promote selective reaction pathways, leading to a higher purity of the desired product.

Recycling a portion of the product stream back into the reactor can help to promote better mixing and heat transfer, which can improve the overall efficiency of the reaction.

In addiction recycling unreacted starting materials or byproducts can reduce the amount of waste generated by the process, which can be beneficial from an environmental and economic standpoint.

5.6. Mixer and splitters

A stream mixer is a device used to mix two or more gas streams together. Gas stream mixers are commonly used in various industrial processes that require precise mixing of gases to achieve specific process conditions.

Gas stream mixers can come in different designs, but most operate by combining the gas streams in a mixing chamber, where the gases are thoroughly mixed to ensure uniform composition. Some mixers may also use a static mixer element, which consists of a series of baffles or vanes that create turbulence and enhance mixing.

Gas stream mixers can be found in a wide range of applications in particular petrochemical industries, as well as in environmental control systems and research laboratories. The mixing of gases can have a significant impact on the efficiency and effectiveness of many industrial processes, making gas stream mixers an essential component in many systems.

On the other hand, a splitter component is a device that is used to divide the gas stream into multiple branches, allowing for different reactions to occur simultaneously in each branch.

Splitter components are commonly used in gas-phase reactions, where it is necessary to control the flow of reactants and products in the reactor. By splitting the gas stream, different reaction conditions can be created in each branch, such as different temperatures, pressures, or catalysts. This allows for more efficient and controlled reactions to take place and can also help to reduce unwanted byproducts or side reactions.

There are different types of splitter components used in gas reactors, such as T-splitters, Y-splitters, and flow distributors. These devices are typically designed to minimize pressure drop and ensure uniform gas flow distribution among the different branches.

Overall, splitter components play an important role in gas reactor design and operation, allowing for greater control and optimization of chemical processes.

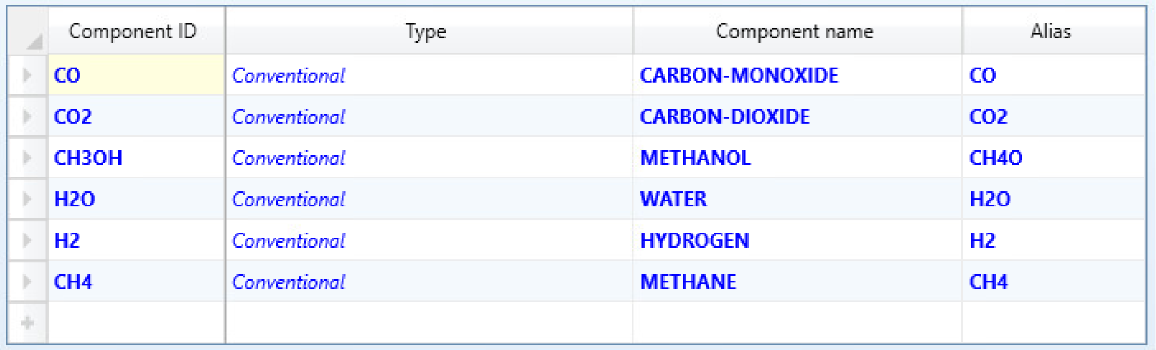
Talking about splitter it's important to define the so called **split fraction** which refers to the ratio of the mass flow rate or volume flow rate of the gas stream that is directed into each of the outlet branches of the splitter. The split fraction is an important parameter in the design and operation of a splitter component, as it determines the relative amounts of reactants that are directed into each branch of the reactor. The split fraction can be controlled by adjusting various parameters such as the geometry of the splitter, the pressure and temperature of the gas stream, and the flow rate of the gas. The goal is to achieve the desired reaction conditions in each branch while maintaining a consistent overall flow rate and composition of the gas stream.

The split fraction can also be used to control the selectivity of a reaction, as different branches of the splitter can be used to introduce different catalysts or reaction conditions to promote specific reactions or minimize unwanted byproducts.

CHAPTER 6: MODEL AND RESULTS

To simulate a catalytic reactor for methanol production in ASPEN Plus as first it must be selected a suitable thermodynamic model, such as the Peng-Robinson equation of state or, in this case, the SRK base method. Choosing a proper thermodynamic model in Aspen Plus is an important step in simulating and analyzing chemical processes accurately. The thermodynamic model you choose will affect the accuracy of your simulation results and the ability to predict the behavior of your system.

Next step is the full characterization of the components that will be involved into the process. For our case the complete list is:



Component ID	Type	Component name	Alias
CO	Conventional	CARBON-MONOXIDE	CO
CO2	Conventional	CARBON-DIOXIDE	CO2
CH3OH	Conventional	METHANOL	CH4O
H2O	Conventional	WATER	H2O
H2	Conventional	HYDROGEN	H2
CH4	Conventional	METHANE	CH4

Figure 6.1: Component list in ASPEN model

6.1. General flowsheet

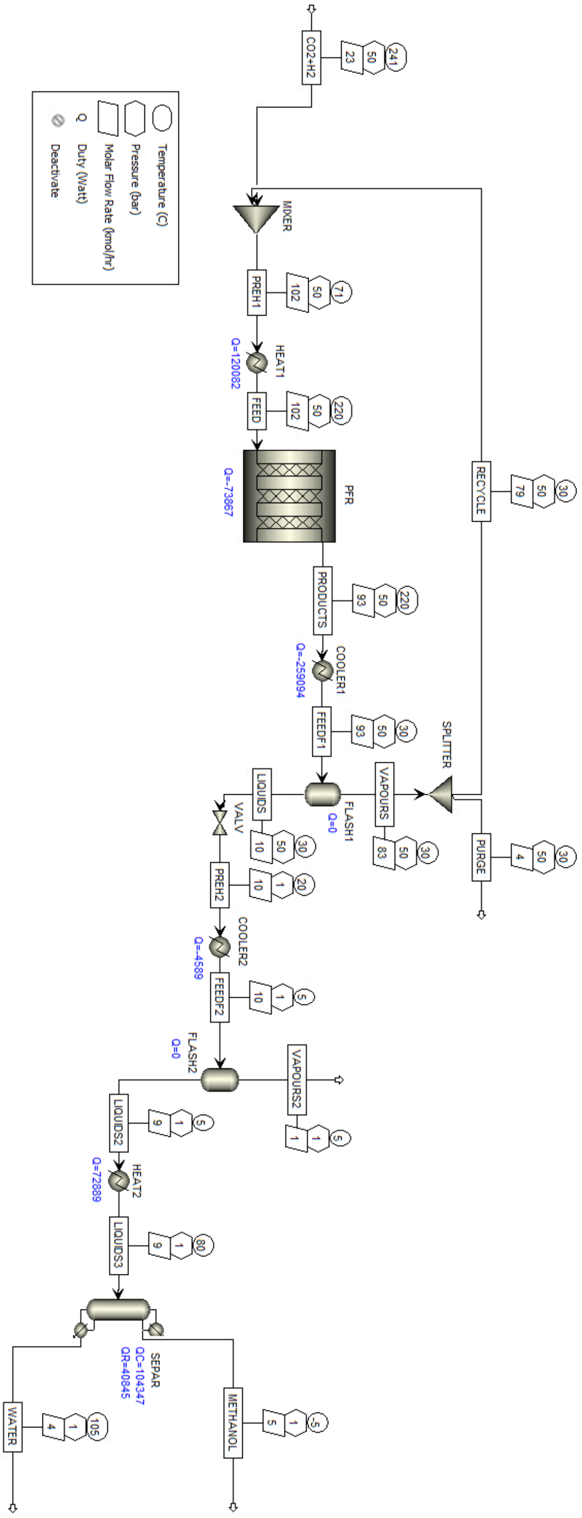


Figure 6.2: Methanol process complete flowsheet

Here it is reported the complete flowsheet for the reactor block and the successive separation process. The stream entering the blocks is the one that comes from the previous electrolysis outgoing stream (‘CO2+H2’ stream) at a temperature of 241°C and pressurized at 50 bar. This flow enters a mixer block with the recycled stream and is sent to HEAT1 where the inlet temperature of the PFR is achieved, in this case 220°C. To correctly model the catalytic reactor the RPlug block on Aspen has been chosen. The outgoing stream PRODUCTS is then sent to a cooler that cools down the stream until the FLASH1 temperature (30°C). Here the stream is separated in terms of phases: vapors, which composition is mainly H2 (molar fraction 0.912), go up in the column and enter the splitter where 95% of the stream is recycled back while the remaining is sent to the purge.

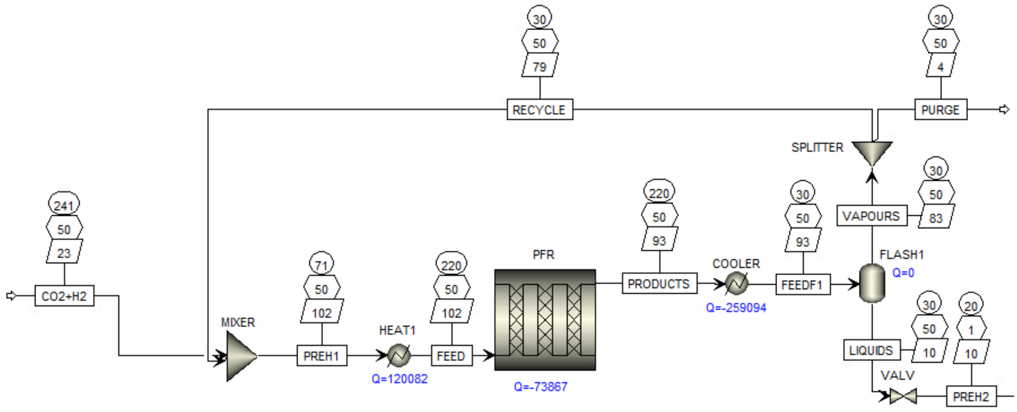


Figure 6.3: Recycle block flowsheet

The opposite stream LIQUIDS now is sent to a valve that decreases its pressure until the atmospheric one and then its cooled down in order to enter the second flash column with a pressure of 1 bar and a temperature of 5°C. Here approximately the 93.3% of the CO2 is here divided in the VAPOURS2 stream while LIQUIDS stream have a molar fraction of 0.492 for water and 0.485 for methanol. The almost total liquid mixture is sent to a second heater that brings the temperature to 80°C and then enters the distillation column represented by a DSTWU block. Number of stages is 15, both the condenser and the reboiler have a pressure of 1.1 bar: the light component is CH3OH, METHANOL stream has 0.954 molar fraction of methanol while WATER stream is 99.95% composed by water (molar).

6.1.1. No-recycle case

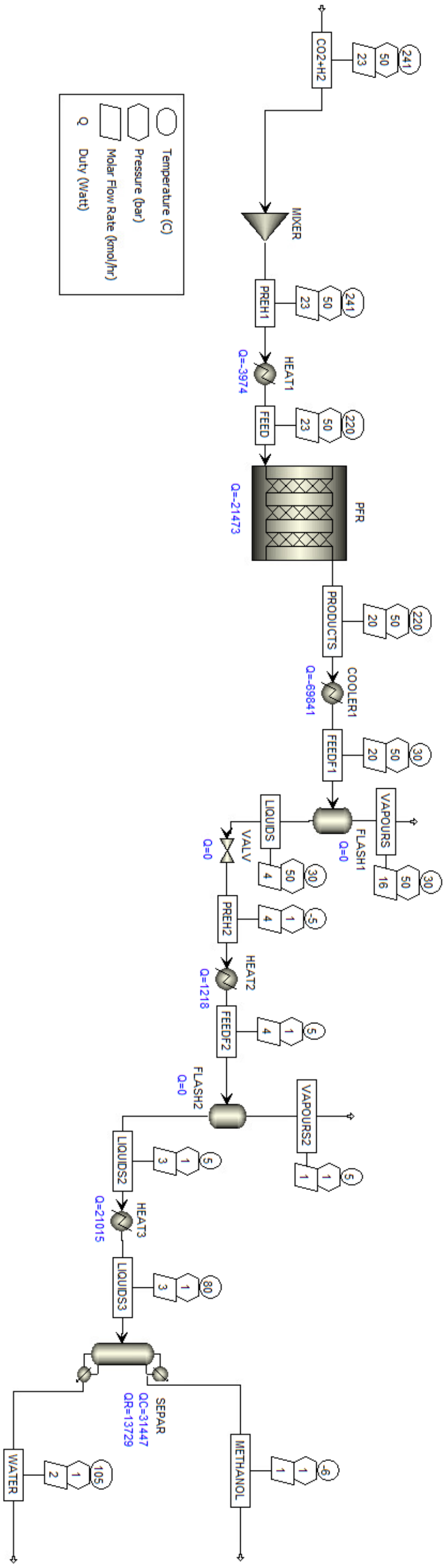


Figure 6.4: No-recycle case complete flowsheet

6.1.2. Sensitivity analysis

Sensitivity analysis is a technique used to determine how changes in an input variable impact the output of a model or system. It involves varying one or more inputs while keeping all other inputs constant, and observing how the output changes as a result.

Sensitivity analysis can be used to evaluate the importance of different input variables to the output of a model or system, identify which inputs have the greatest impact on the output, and which have the least. This type of proceeding determines the range of input values that produce acceptable or optimal output values.

Here will be shown four different sensitivity analysis that compare two different configurations. Recycle and no-recycle flowsheets will be compared both with the same operational condition. The results of sensitivities show the behavior of selectivity, conversion and yield as a function of reactor length, tubes number, split fraction and PFR temperature.

The first one is **split ratio** sensitivity analysis, realized for obvious reasons only for recycle model:

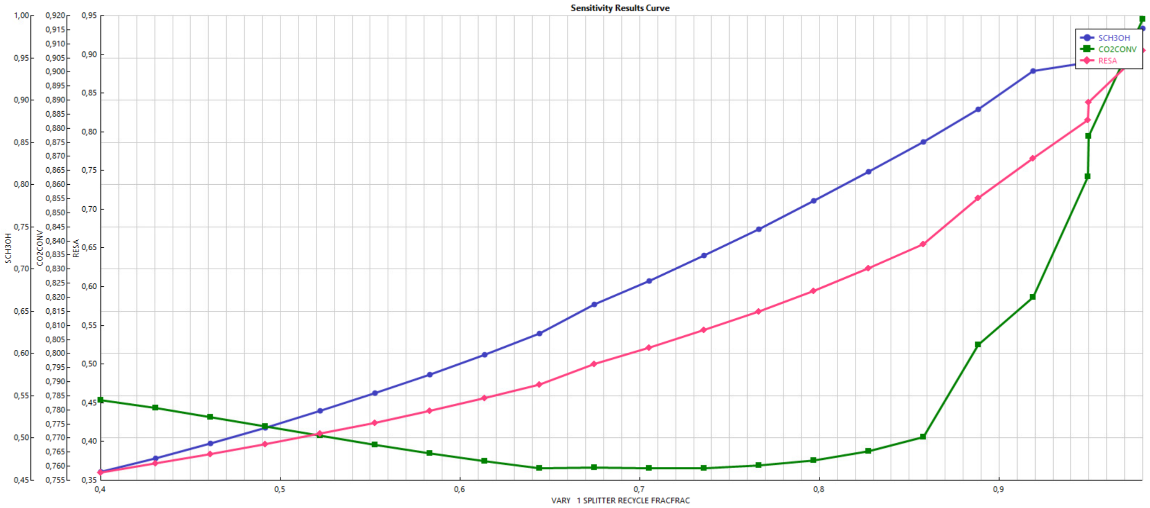


Figure 6.5: Split fraction sensitivity analysis for recycle case

We can appreciate an increasing trend of the reaction yield with increasing split fraction value. This could be considered as a general behavior because recycling more unreacted gas back to the reactor increases the concentration of reactants, which in turn drives the reaction forward to produce more methanol. However, there is a limit to the amount of gas that can be recycled back to the reactor before it becomes counterproductive. If too much gas is recycled, it can lead to a buildup of inert gases that can reduce the concentration of reactants and decrease the yield of the reaction.

There are several ways to maximize the split ratio in a methanol production plant. As first the capacity of the recycle compressor can be increased to recycle more unreacted gas back to the reactor. Alternately, the reactor operating conditions such as temperature, pressure, and flow rate can be optimized to ensure that the reaction is proceeding at the highest possible rate. The efficiency of the catalyst used in the reactor can be improved to increase the rate of the reaction. It is important to ensure that gas leakages or any possible impurities are minimized to maximize the amount of gas available for recycling.

The second sensitivity analysis is carried out varying le **length of the tube** from 0.1 m to 10m.

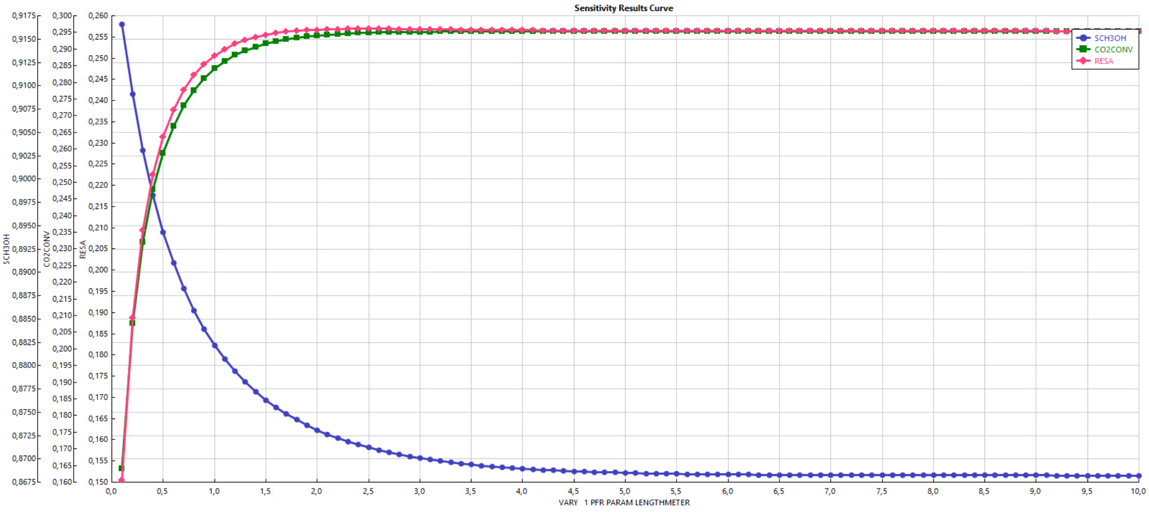


Figure 6.6: Length sensitivity analysis for no-recycle case

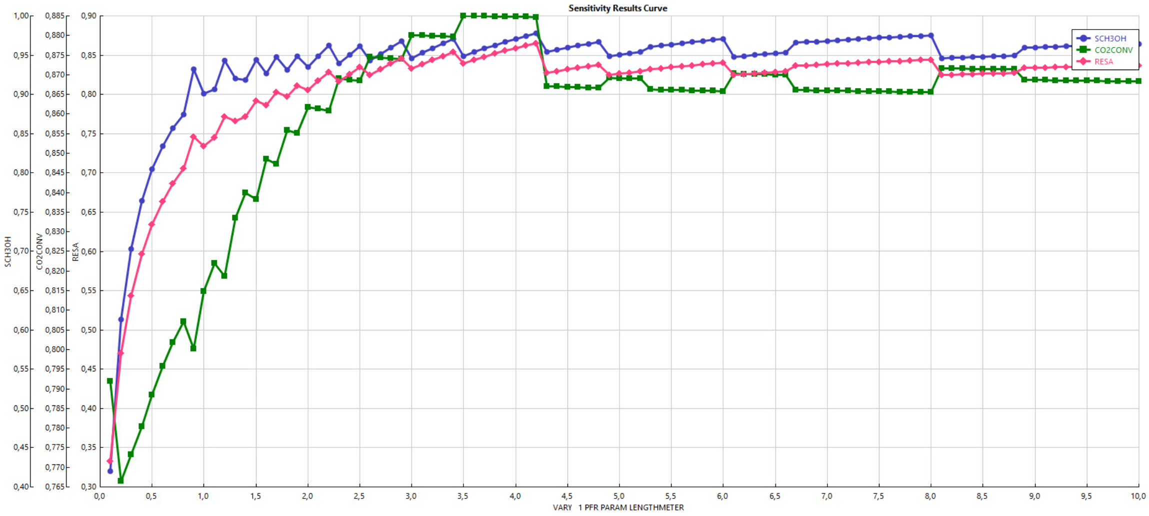


Figure 6.7: Length sensitivity analysis for recycle case

Selectivity has a decreasing trend in the no-recycle model starting from an approximate value of 0.917. Yield (pink trend) confirms higher values in recycle model, the same for conversion. At 2 meters in the no-recycle case a sort of stabilization for yield and conversion values is appreciated. In general, the length of the tubes in the reactor has an impact on the yield, selectivity, and conversion of the reaction. In fact, the tubes in the reactor are used to house the catalyst that is responsible for converting the reactants into methanol. The effect of tube length on yield, selectivity, and conversion is mainly due to the impact it has on the residence time of the reactants within the reactor. The residence time refers to the length of time that the reactants spend within the reactor, and it is an important factor in determining the efficiency of the reaction. Increasing the length of the tubes in the reactor can increase the residence time of the reactants. As we can see in our results, this can lead to an increase in conversion, as the reactants have more time to meet the catalyst and react to form methanol. On the other hand, increasing the residence time can also result in a decrease in selectivity, as the longer residence time can lead to unwanted side reactions and this effect is visible in the no-recycle case. There is a trade-off between yield, selectivity, and conversion when considering the effect of tube length in a methanol production plant, the optimal tube length will depend on the specific operating conditions of the plant and the desired balance between yield, selectivity, and conversion.

The third analysis is carried out for **tubes number** varying into 1-40 interval and these are the results:

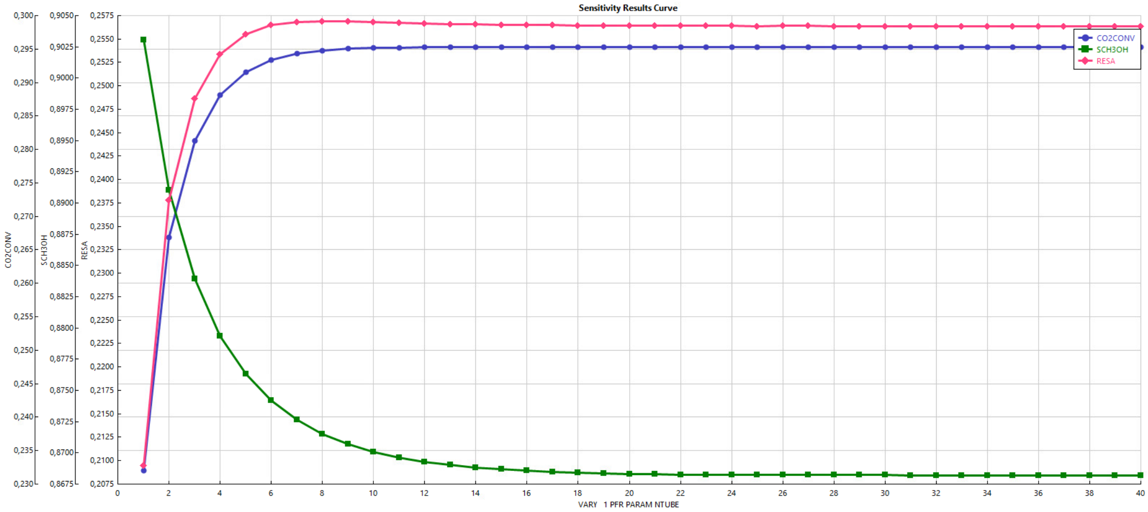


Figure 6.8: Tubes number sensitivity analysis for no-recycle case

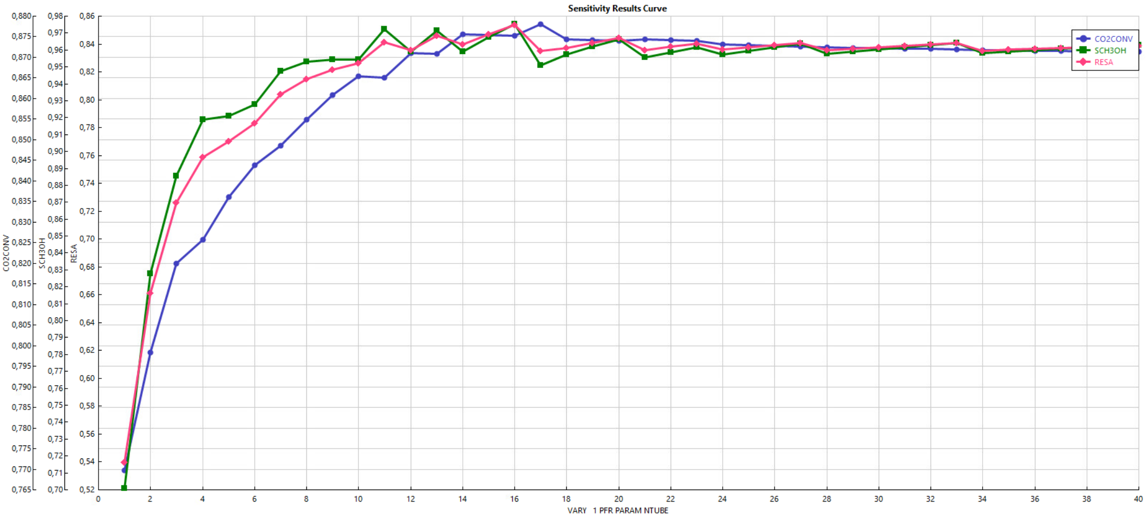


Figure 6.9: Tubes number sensitivity analysis for recycle case

Selectivity trend is similar for both cases compared to length analysis, higher yield values are registered in the recycle case. In the first case both yield and conversion appear to stabilize at 7 tubes configuration. The number of tubes is another parameter that goes to modify yield, selectivity, and conversion of the reaction due to the impact it has on the available surface area for the reaction. Increasing the number of tubes can increase the available surface area for the reaction, which can increase the rate of the reaction and therefore the conversion. However, increasing the number of tubes can also lead to a decrease in selectivity, as there is a higher likelihood of unwanted side reactions occurring. Both these effect are quite evident in the no-recycle case.

Finally, the analysis for PFR operative **temperature** realized for 200°C-260°C interval:

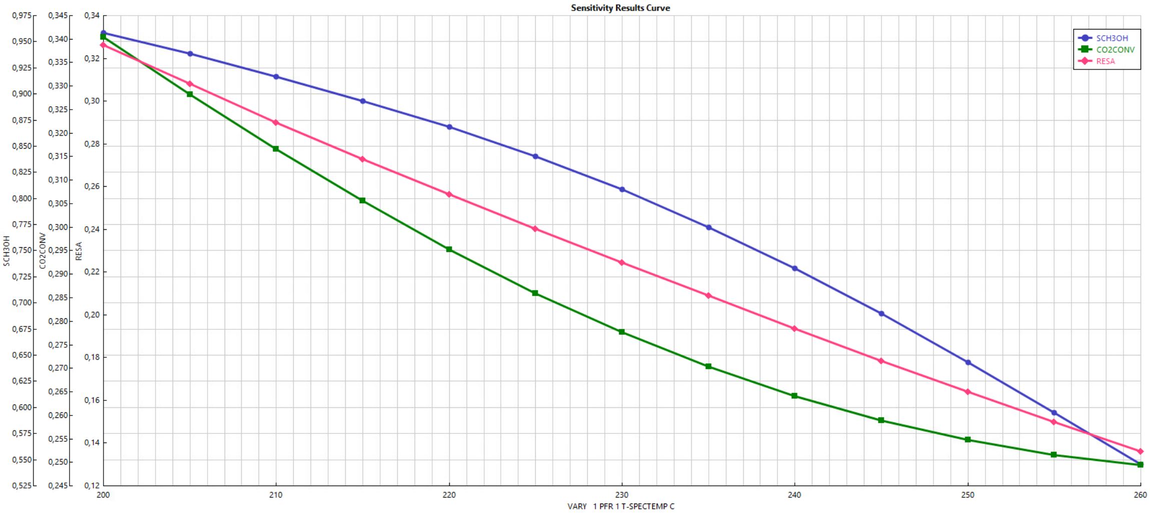


Figure 6.10: PFR temperature sensitivity analysis for no-recycle case

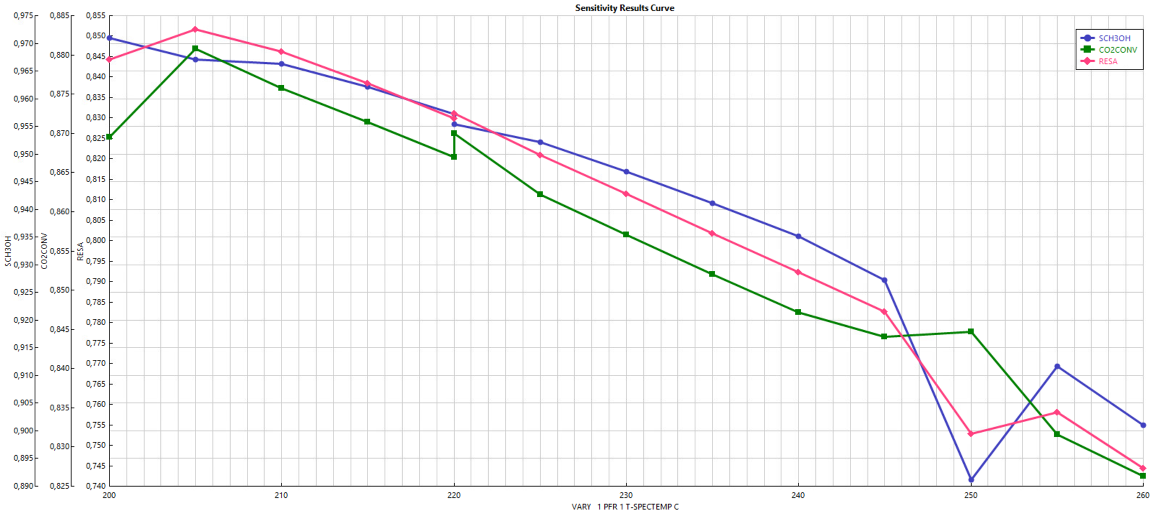


Figure 6.11: PFR temperature sensitivity analysis for recycle case

Trends are evident for both cases: increasing temperature means decreasing yield, selectivity and conversion. Reactor temperature has a huge impact on the reaction rate as it is favored by an increase in temperature, in general thermodynamic equilibrium conditions are strictly dependent on temperature variations. On the other methanol production reaction is exothermal, increasing temperature means to bring a negative impact on it and to reduce the maximum yield achievable. Increasing the reactor temperature can also lead to a decrease in selectivity, as higher temperatures can promote unwanted side reactions that can reduce the yield of methanol.

6.2. Efficiency evaluation

For the evaluation of the overall efficiency of the plant all the electric and thermal costs from both the electrolysis and catalytic reactor blocks are accounted for.

As first the electrical expense related to electrolysis block the is required. We use the efficiency definition that relates the produced amount of hydrogen, heating value and the electric power.

$$\eta_{electrolysis} = \frac{q_{H2} LHV_{H2}}{P_{electrolysis}} \tag{42}$$

with:

$q_{H2} = 34.5582\ kg/hr$

$LHV_{H2} = 33.33\ kWh/kg$

$\eta_{electrolysis} = 0.6$ (value taken from bibliography for alkaline electrolyzer) this leads to an electric power equal to:

$$P_{electrolysis} = \frac{q_{H2} LHV_{H2}}{\eta_{electrolysis}} = 1.92\ MW$$

The overall efficiency will be expressed as Eq.(43):

$$\eta_{CH3OH} = \frac{q_{CH3OH}\, LHV_{CH3OH}}{P_{pump} + P_{electrolysis} + P_{CO2compr} + P_{compress} + P_{heat1} + P_{heat2} + P_{reb}}$$

with:

$q_{CH3OH} = 140.225\ kg/hr$

$LHV_{CH3OH} = 19.93\ MJ/kg$

$P_{pump} = 0.262\ kW$

$P_{electrolysis} = 1.92\ MW$

$P_{CO2compr} = 14.6\ kW$

$P_{compress} = 42.774\ kW$

$P_{heat1} = 121.5\ kW$

$P_{heat2} = 73.2\ kW$

$P_{reb} = 40.93\ kW$

From all of this, the result is:

$$\eta_{CH3OH} = 0.35$$

The general efficiency of a methanol production plant is influenced by various factors, including the type of feedstock, the reactor design, the catalyst used, and the operating conditions.

CONCLUSIONS

The use of CO2 capture and water alkaline electrolysis offers a promising pathway to produce methanol, which can be used as a clean energy source and chemical feedstock. The efficiency and sustainability of methanol production from CO2 capture and water alkaline electrolysis depend on several factors, such as the efficiency of the capture and electrolysis processes, the purity and quality of the feedstocks, and the optimization of operating conditions.

Methanol production from CO2 capture and water alkaline electrolysis can play a crucial role in the transition towards a sustainable and low-carbon economy by providing an alternative to fossil fuels and reducing the dependence on non-renewable resources. The integration of methanol production with other renewable energy sources, such as wind and solar, can enhance the sustainability of the overall process and improve the economics of methanol production.

The life cycle assessment of methanol production from CO2 capture and water alkaline electrolysis should consider the environmental impacts associated with the entire process, including the upstream and downstream activities, to ensure that the process is truly sustainable.

The development of advanced catalysts and process improvements could help to enhance the selectivity, yield, and energy efficiency of methanol production from CO2 capture and water alkaline electrolysis, making it a more attractive and viable technology for commercial-scale production.

The economic feasibility of methanol production from CO2 capture and water alkaline electrolysis depends on various factors, such as the availability and cost of feedstocks, the scale of production, and the market demand for methanol.

The future of methanol production from CO2 capture and water alkaline electrolysis is promising, but further research and development are needed to overcome technical, economic, and environmental challenges and to realize the full potential of this technology.

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