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# Experimental investigation of the CO<sub>2</sub>/CH<sub>4</sub> gas mixture separation via membrane separation process

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A mio padre: uomo instancabile e resiliente. Mio unico ed eterno amore.

## **1** General introduction

Intergovernmental Panel Climate Change (IPCC) Fifth Assessment Report has reported that the anthropological activities are the major contributors to the rise of the Earth's surface temperature. In particular, it experienced 0.85°C rise between 1880 and 2012 [1] leading the passage from Holocene geological era to the Anthropocene's one. Consequently, the response to the climate change cannot be based only on one sector but it needs a strong interaction between various levels. The rise in global CO<sub>2</sub> concentrations has reached 20 ppm per decade that is 10 times higher than that experienced during the past 800.000 years [2].

According to IPCC report, the 20-40% of the entire population has experienced the temperature rising of  $1.5^{\circ}$ C in at least one season. This leads to different consequences as regard as ecosystem integrity that includes an increasing number of extreme weather events such as, droughts, floods, sea level rise, hurricanes and biodiversity loss. One of the main points to be underlined is that the most affected people belong to the low- and middle-income countries because they have seen a very strong decline in food, energy and water securities, main pillars of sustainable development goals. It leads to the boom of migration that is a big deal of our epoque [3]. Furthermore, the global economic growth and the change in lifestyle habits have caused not only the environmental degradation but also a profound gap between the rich part of the world that is becoming more and more rich and the poor's one that is indeed becoming more and more poor[4]–[7]. The increasing utilization of fossil fuels in different sectors is the crucial actor in greenhouse gas emissions [8] [9].

Another important factor contributing to the increase of GHG emissions and so, to the climate change is the utilization of natural land with its management. But differently from use of fossil fuels, land ecosystems are also a sink of GHG emissions. It is also true that the world actual emissions are far away from the possibility to be totally absorbed by natural sink, but this is the main reason why in the Nationally Determined Contributions (NDCs) of the parties to the Paris Agreement they cover a dominant role. Land is the key factor to the survival of species because it proves food and energy and freshwater. Moreover it has to be considered that it is a pain relief for human psychological insights: it has been found that people living in seminatural or natural environments show less mortality, less heart's diseases and less depression [10].

Finally, as regard as coasts they represent the most densely populated areas on Earth, and it is mainly due to the fact that the contact with water make the land more productive for any activity sectors. Also, the ancients were used to stabilize their habitats near fluvial or coastal zones. It is worthwhile to note that the climate change can have a severe impact to populations living near water and according to Shared Socioeconomic Pathways (SSPs) by 2050 they will increase to more than one billion against the actual 680 million people[11] [12]. If there will be no actions against climate change, the cost to cover the disasters will be much higher than the initial investment to prevent them. According to IPCC studies, it would cost the global economy 428 billion USD yr<sup>-1</sup> by 2050, and 1.979 trillion USD yr<sup>-1</sup> by 2100 in the first case. In the second case, it could save more than a trillion dollars USD yr<sup>-1</sup> by 2100 [13].

In the same way, the rise of the sea level sea from 25 to 123 cm by 2100 without adaptation will lead to 0.2-4.6% of the global population impacted by coastal flooding annually, with average annual losses amounting to 0.3-9.3% of global GDP. Indeed if the investments would be done in order to prevent it number of people flooded and the losses caused will decrease about 2 order of magnitude [14] [15].

## 1.1 Global warming of 1.5°C

Global 'warming' has been defined by IPCC as an increase of global mean surface temperature (GMST) above pre-industrial levels<sup>1</sup>. More in specific, warming in one point is the combination of temperatures of land surface air and sea surface for a 30-year period and its value is compared with a reference period 1850-1900. The trend is projected through the following years and the future is forecasted according some criterion [16]. As shown Figure 1-1 elaborated from IPCC reports the human activities have provoked 1.0°C of global warming above pre-industrial levels, with a *likely* range of 0.8°C to 1.2°C. With a high level of confidence<sup>2</sup>, if the

<sup>&</sup>lt;sup>1</sup> The multi-century period prior to the onset of large-scale industrial activity around 1750. The reference period 1850–1900 is used to approximate pre-industrial GMST.

<sup>&</sup>lt;sup>2</sup> A level of confidence is expressed using five qualifiers: very low, low, medium, high and very high, and typeset in italics, e.g., medium confidence. The following terms have been used to indicate the assessed likelihood of an

global warming continues to show this trend it could reach 1.5°C between 2030 and 2052.



Figure 1–1 Observed monthly global mean surface temperature. The orange dashed arrow shows the time period at which the 1.5 °C rise temperature will be reached following the actual trend represented in orange line. The grey plume is the projection of temperature if the  $CO_2$  emissions follow a straight line from 2020 to reach net zero by 2055. They blue plume indeed shows the effect of faster policies in curbing  $CO_2$  emissions, reaching net zero in 2040. Finally, the purple plume shows the response of global warming if the zero net  $CO_2$  would be reached after 2055 [16].

The impact to human life and ecosystems in general will be weaker if the raise is limited to 1.5°C instead of 2°C, but higher in both cases than at present. Naturally, it depends on geographic location, infrastructure's reliability and policy measures for mitigation. In particular, it could lead to heavy precipitations or long period of droughts. Or even, increase of health diseases, lack of water and food. It follows that the mitigations policies are needed and essential to limit irreversible disasters [17].

## 1.2 CO<sub>2</sub> emissions: actual trend

The European Union has promoted different policies to try to mitigate and stop climate change: to curb CO<sub>2</sub> emissions of 30% by 2030 but still has to be approved the reduction of at least 40% by 2050 compared to preindustrial levels to reach a

outcome: virtually certain 99–100% probability, very likely 90–100%, likely 66–100%, about as likely as not 33– 66%, unlikely 0–33%, very unlikely 0–10%, exceptionally unlikely 0–1%. Assessed likelihood is typeset in italics, e.g., very likely.

climate neutral EU. Beyond the EU, all Parties to the Paris Agreement are required to prepare emissions reduction pledges, the ones that are previously mentioned as Nationally Determined Contributions. The Paris Agreement sets some rules that have to be respected from all Parties in order to determine the state of national greenhouse gas emissions and the progress reached by implementing different measures of NDCs. The Emissions Database for Global Atmospheric Research (EDGAR) estimates the global annual emissions for a wide range of anthropogenic activities giving the possibility to verify the methodology that is I line with the most recent literature but also with the IPCC recommendations.

The global annual emissions of fossil  $CO_2$  in Gt  $CO_2$  yr<sup>-1</sup> are illustrated in Figure 1-2 for the entire time series of the EDGAR database (1970-2019). The examined activities are:

- Power industry: it includes power and heat generations plants being either public or individual producers.
- Other industrial combustion: it refers to industrial manufacturing and production of fuel.
- Buildings: they can be of whatever nature both public and private.
- Transport: it includes road transport, non-road transport, domestic and international aviation and international shipping.
- Other sectors: it contains all the activities that produce emissions but that cannot be accounted in the previous categories.



Figure 1-2 Total global annual emissions of fossil CO2 in Gt CO2 yr<sup>-1</sup> by sector [18].

Even if policies to cut  $CO_2$  emissions have been established, its trend has continuously rose. In particular, the average yearly C increase into the atmosphere is 4 PgC yr<sup>-1</sup> that corresponds to ~15 Gton  $CO^2$  yr<sup>-1</sup> and the resulting  $CO_2$ concentration in the atmosphere increases with a rate of ~2 ppm yr<sup>-1</sup> (the assumption is that the atmosphere is an 8 km thick layer surrounding the Earth's sphere, whose radius is 6371 km).

However, an abrupt trend change has been experienced in 2020. In fact, global carbon dioxide emissions fell by 6.4%, as the COVID-19 pandemic obliged to behavioural and lifestyle changes in each sector and activity. economic and social activities worldwide, according to new data on daily fossil fuel emissions. The most outstanding result is reported by United States of America that experiences a reduction of about 12.9% with respect to 2019. It has followed by India with its -8% and Europe with -7.7% according to ©nature research. China has shown a different trend with respect other countries since it was the first to face the virus and so, also the first at fixing rules such as lock down and other measures. So, after an initial reduction in  $CO_2$  emissions it has recovered as fast as possible its economy and so, also its emissions. The Figure 1-3 explains in a bar chart as previously mentioned [19].



Figure 1-3 Comparison between annual CO<sub>2</sub> emissions in 2019 and 2020 in major countries and in the entire world [19].

### 1.3 CO<sub>2</sub> emissions: future trend

The current policies will show their impact on reducing future warming and so, only scenarios can be predicted to understand their effectiveness. In particular, Figure 1-4 elaborated by Robbie Andrew, senior researcher at the Center for International Climate Research (CICERO), mapped out the global emissions reduction scenarios necessary to limit global average warming to 1.5°C and 2°C [20], [21], that are:

- No climate policies scenario: this would lead to a rise between 4.1°C and 4.8°C of global mean surface temperature if emissions are not regulated and continue to rise as nowadays.
- Current policies scenario: it shows that a rise of about 3°C could be experienced if only the actual policies are applied without any additions.
- Pledges and targets scenario: it forecasts an increase of maximum 2.8°C if all the parties of Paris Agreement would respect their established pathway to curb emissions.
- 2°C pathways: strong policies must be adopted to reach this target.
- 1.5°C pathways: it could preserve major part of actual ecosystems, but a very big effort must be made by policy makers.

These curves, with their interval of confidence, show that reductions in emissions would be needed to achieve 2°C or 1.5°C. And if the peak in emissions will be far away in time, more difficult will be the recovery [22].



Figure 1-4 Global greenhouse gas emissions and warming scenario [22].

It is also important to underline that future CO<sub>2</sub> emissions coming from energy sector cannot be limited in an easy way. In fact, despite all the policies focused on curbing GHG emissions, the number of fossil fuel plants is arising more and more in the last decades. This is since the global population is increasing but also the social wellness that led to an energy and resource-intensive lifestyle. More in detail, the existing power plant not only are emitting in present days, but they will emit during their entire lifetime that usually is around 30 years.

Figure 1-5 elaborated by International Energy Agency shows that the global cumulative CO<sub>2</sub> emissions coming from existing power plant calculated in the period 2019-2070 will account for more than 2/3 of the admissible emissions according to the Sustainable Development Scenario. So, to curb future CO<sub>2</sub> emissions, not only it is necessary to build low-carbon power plants (e.g., based on renewables) but also to retrofit existing power plants with carbon capture devices since the anticipated retirement is not economical feasible. Concerning new fossil power plants, they should include a carbon capture section as part of their original design.





# 2 Key solutions for decarbonization

The energy sector is the principal origin of the global emissions and, consequently, it is also as first in charge of solving the world climate challenge. The International Energy Agency has proposed the Net-Zero Emission plan by 2050 that expect to totally cut CO<sub>2</sub> emissions by 2050. The measures included in the plan along with the reduction of GHG emission from non-energy sectors aim to limit the rise of global temperature to 1.5 °C. Nevertheless, the NZE is only one of the available solutions to reach the aim. In fact, for instance, much depends on the pace of development and innovation in new technologies, the commitment of citizen willing to change behaviour, the availability of sustainable bioenergy and the power and the efficacy of international collaboration.

In order to reach the quick reduction in CO<sub>2</sub> emissions over the next 30 years, the NZE involves a wide range of policy approaches and technologies. The key pillars of decarbonisation of the global energy system are [24]:

- Energy efficiency. It is widely recognised that increasing the technological performances in each energy sector is useful to firstly reduce the amount of required abiotic resources input but also to cut the emissions. In the construction sector, the retrofitting of existing building in combination with new constructions zero-carbon-ready are fundamental for improving energy efficiency. In transport sector, both the switch from fossil fuels to biofuels in public and private and the shift from ICE to electrical vehicles are promising for energy efficiency improvement. In the industry sector, even if the technological performances are good enough, energy system managements or better equipment's (e.g., electric motor or heaters) can represent excellent drivers.
- Behavioural changes. According to IEA study, the citizen contribution for decarbonization can account for 8%. It regards daily life change starting from lowering the temperature set point for both heating and cooling, the preference of trainline with respect to airplane for covering short distances, the use of green mobility, the increment of recycling or even to limit the speed in highways. It is evident that a big effort must be sustained by government to improve the existing mobility infrastructure.
- Electrification. The increasing share of renewable technologies for providing energy must be followed by the electrification of end-users. In fact, wind energy or solar energy are converted in most of the cases in electricity. So, that the production, transmission, and utilization of energy is fully electric. Most of domestic utilities are still electrified but the heating/cooling are still in run. Electric vehicles represent another mean to reach the total

electrification. But it can determine peak of demand that can lead to instability: demand-side management or the use of low emission sources (e.g., hydropower) will cover this problem.

- Renewables. For decades, the major source of renewable energy has been the hydropower, but solar and wind power will have a dominant role. The other renewables such as concentrated solar power, geothermal, bioenergy will be important to ensure electricity security, energy storage and reliable electricity network. The appliances could be different going from electricity to feed electrical vehicles or to feed electrical boiler or chiller.
- Hydrogen and hydrogen-based fuels. It is a platform molecule to produce syngas but also to be injected in pipeline with natural gas for feeding households 'appliances. In general, hydrogen can be used in fuel cells for producing electricity but also to store it. This technology is expensive but the widespread use of hydrogen also for fuel can lead to lower the cost.
- Bioenergy. Until now, the demand of bioenergy has been confined in biomass as wood for cooking, but it is not a clean technology since its combustion has led to premature deaths. In general, the use of sustainable bioenergy (e.g., wastes) can lead to decarbonisation. Care has to be taken as regard as biomass since its depletion rate must not exceed it regeneration one. Biogas coming from anaerobic digester will be one the main renewable source for cooking. Bioenergy such as biomethane or bio-oil can use the existing infrastructure: the former can use the existing pipeline for natural gas whereas the latter can use oil distribution networks. The major use of liquid biofuel will be on shipping and aviation since the terrestrial mobility will be dominated by electricity.

#### 2.1 Carbon Capture, Utilisation and Storage

Carbon Capture Utilization and Storage ca be accounted for not the solution but as an interim solution since it can recover the CO<sub>2</sub> emissions from already existing fossil fuel power plants. Some researchers state that it is not a feasible solution from economic point of view, others affirm that the energetic cost of this kind of technology produce more emissions than those recovered. A lot of pilot plants worldwide is testing the effectiveness of that technology. Until now, it constitutes the only solution to overcome the problem of carbon lock-in because the dismissing of existing power plants is economically unfeasible. To make an example, Germany's plane to retire around 40 GW of coal-fired plants before 2038 is accompanied by a lot of incentives to compensate the losses of coal mines and power plants owners but also to support the communities that will be affected by this decision.

It is also relevant to note that the renewable penetrations in energy market cannot substitute all the existing fossil fuel-based generation. This is due to main reasons: first, technologies based on renewable resources does not provide enough inertia like fossil-fuel power plants; secondly, renewables are strictly related to weather conditions and so, if storage systems continue to take time to enter in the market, the energy demand could not be satisfied continuously. It follows that the world must still relay on fossil-fuel power plants and so, CCUS is the only way to make them less dangerous and impacting.

The term utilization and storage reflect the fact that once the carbon dioxide emissions are captured, they can be used as feedstock in synthetic fuels for or permanently stored to achieve negative emissions.

The Net zero emission scenario elaborated by IEA forecasts that different measures will be taken for implementing CCUS and it estimates that 1670 Mt CO<sub>2</sub> will be captured by 2030 and 7600 by 2050 against the actual 40 as shown in Table 2-1. More in detail, it divides the CO<sub>2</sub> captured according the different resources: fossil fuels and bioenergy. As it can be expected, the CO<sub>2</sub> captured from the formers are higher than the latter since the actual market is relying on that. The direct air capture removal is not an efficient technology so that, its contribution is very low compared to the others two.

	2020	2030	2050
Total CO2 captured (Mt CO2)	40	1670	7600
CO2 captured from fossil fuels and	39	1325	5245
processes			
Power	3	340	860
Industry	3	360	2620
Merchant hydrogen production	3	455	1355
Non-biofuels production	30	170	410
CO <sub>2</sub> captured from	1	255	1380
bioenergy			

570
180
625
985
630

Table 2-1 Key global milestones for CCUS [24].

In the market there are different CO<sub>2</sub> capture technologies, and their applications depend on different parameters such as initial and final CO<sub>2</sub> concentrations or ease of integration with existing infrastructure, economic considerations pr operating pressure and temperature. In the next chapter on overview on the actual technologies for CO2 separations are described with particular focus on that used for natural gas purification [23].

#### 2.1.1 CO<sub>2</sub>-Enhanced recovery from natural gas hydrates

As previously said, the carbon capture, utilisation and storage have to be part of mitigation measures to reach net zero emissions by 2050 and to limit global warming. In this context, great attention is put on underground storages that can be of different types. But it is important to understand that once the CO<sub>2</sub> is stored it has to be monitored through the year because an accidental release in the atmosphere can be very dangerous since the inhalation can lead to rapid death [25]. The main types of underground storage site are oil and gas wells, coal beds too deep to be mined, brine aquifer and natural gas hydrate. The common denominator is that the CO<sub>2</sub> is trapped into the reservoir and it goes to substitute other molecules that in natural gas hydrates is mainly methane, CH<sub>4</sub>.

In particular, natural gas hydrates are solid ice-like substances formed from water when the natural gas (e.g., mainly methane) combines with water under highpressure (>0.6MPa) and low-temperature conditions (<300K) via hydrogen bonding [26] [27]. Each standard cubic meter of NGH can result in approximately 160–180 cubic meters of natural gas under normal conditions [28]. Figure 2-1 displays the detailed information on the hydrate crystal cell structure with methane as reference molecule. As can be seen, a molecule of methane is surrounded by water molecules. The key concept is the replacement of natural gas molecules (as previously said, mainly methane) with the captured CO<sub>2</sub> that will become stored.



Figure 2-1 Simple schematic of common unit crystal structures of the gas hydrates.

The procedures leading to exploitation of a gas hydrate to obtain methane are mainly four [29]: depressurization, thermal stimulation, chemical injection and gas swapping. As regard as depressurization, it consists of lowering the pressure inside the hydrates so that it becomes thermodynamically unstable and decomposes thanks to the geothermal heat flow set free by the same decomposition. The best operating conditions are high temperature and high geothermal heat flux [30]. Indeed, the thermal stimulation tries to raise the hydrate temperature above the stability point in order to let hydrate dissociate but it is energy consuming since it has to overcome the endothermic heat of dissociation [31]. Chemical injection consists of the injection of organic or inorganic compound to let hydrate dissociate. The main drawback is that the dissociation lowers the temperature and so an energy source is needed to maintain the equilibrium. Finally, the most relevant and the reason why that study is conducted is the gas swapping. It involves injecting a guest molecule into the gas hydrate reservoir. In particular, CO<sub>2</sub> is injected in this reservoir substituting the natural gas that is released as fluid. So, there is a double vantage: from one hand, the CO<sub>2</sub> is sequestered but on the other hand, molecules of CH<sub>4</sub> are liberated.

Furthermore, the molecule of CO<sub>2</sub> can create at the same temperature a stable hydrate structure at lower pressure conditions than CH<sub>4</sub> molecules and, it can give a more mechanical stability since it is a bigger molecule. This leads to lower the risk of rock failure of the reservoir.

Another interesting reason is that the CO<sub>2</sub> hydrate formation is exothermic, and this heat is useful to enhance natural gas hydrates to dissociate, since the heat of CO<sub>2</sub> hydrate formation is higher than the heat of CH<sub>4</sub> hydrate dissociation. In particular:

$$CO_{2(g)}$$
 + nH2O →  $CO_2$  (H2O)<sub>n</sub> ΔH<sub>f</sub> = − 57.98 kJ/mo  
CH<sub>4</sub> (H2O)<sub>n</sub> → CH<sub>4(g)</sub> + nH2O ΔH<sub>f</sub> = 54.49 kJ/mol

The main drawback is that the production rate in this method is very low due to the fact that the CO<sub>2</sub> molecules lowers the fugacity of CH<sub>4</sub> that represents the main goal [32]. Table 2–2provides the main advantages and disadvantages of all types of gas hydrate production methods.

Method	Advantages	Disadvantages	
Depressurising	No need to input excess energy	Resulting in ground subsidence and submarine	
	Having potential to use in gas hydrate	landslides	
	reservoirs with low hydrate saturation,	Hydrate reformation may occur due to	
	high porosity, and low free gas	endothermic depressurisation	
		Production of water	
Thermal	Production rate can be controlled by	Slow production rate	
Stimulation	changing the rate of injected heat	Inefficient (high heat losses)	
		Costly	
Chemical	Production rate can be improved in a	Not feasible to use in gas hydrate reservoirs with	
Injection	short time period	low permeability	
		Environmental issues	
		Costly	
		Thermal adjustment	
Gas Swapping	Good strategy for $CO_2$ capture and	Not feasible to use in gas hydrate reservoirs with	
	sequestration	low permeability	
		Environmental issues	
		Costly	
		Slow production rate	

Table 2-2 Advantages and disadvantages of four types of gas hydrate decompositions.

Even if the  $CO_2$ -CH<sub>4</sub> exchange in methane hydrates is enhanced due to the previously said thermodynamic aspects, the continuous  $CO_2$  replacement above the surface limit its passage into deeper layers so, lowering the replacement process. In fact, as assed by Cannone S. et al., the storage efficiency defined as the ratio between the moles of  $CO_2$  permanently stored into the NGH and the total amount of  $CO_2$  injected inside the deposit is around 36% [25]. According to his study the syngas produced during the methane extraction and simultaneous carbon dioxide sequestration from the NGH reservoir might contain 64% of  $CO_2$ .

From that the necessity to use upgrading technologies to let the methane reach pipeline quality standards and so, make it free from  $CO_2$  content. This is the reason why next chapters are focuses on natural gas purification technologies existing on the market with particular focus on membranes. In fact, a two-stage membrane (Figure 2-2) can obtain a retentate with 98% CH<sub>4</sub> purity.



Figure 2-2. Membrane process for natural gas sweetening produced via depressurisation and CO<sub>2</sub> replacement [25].

# **3 Natural Gas Purification Technologies**

In this chapter are reviewed all the upgrading technologies for natural gas: even if decarbonisation policies try to shift energy production towards the use of renewable energy sources, it results clear that a bridge is necessary to help the transition. More in specific, the natural gas can be considered as an interim solution and for this reason the above-mentioned natural gas hydrates can be very useful for this purpose: meanwhile they capture carbon dioxide molecules they also provide the needed natural gas for energy transition. Furthermore, with respect to oil and coal the natural gas can be considered as a clean fuel since at parity of produced energy it emits much lower than its competitors. Besides that, natural gas feed power plants can represent the solution to the growing penetration of renewable technologies since they have a high inertia but also provide fast responses to short term demand fluctuations [33].

It must be noted that the global demand of natural gas trend is continuously rising also in the forecast due to the rebound effect as published by IEA (Graph 3-1). Only a decrease has been experienced during the pandemic. This remark the fact that the world still relies on natural gas and the switch to renewable resources cannot be instantaneous but gradual. In support of this thesis, it has to noted that the industrial sector provides the largest contribution to the 2021 recovery in global gas demand, maintains a leading role in the following years [34] and so an abrupt change in demand could have strong repercussions not only in the economic layer but also in social one operating in in this sector. As regard as the natural gas composition, it depends on several parameters such as geographic location of reservoirs, depth, and type. In general, it is formed by 70–90% of methane and the remining part from heavier or lighter hydrocarbons [35]. It follows that the conventional technologies used for natural gas purification coming from well reservoirs can be adapted for that coming from hydrates. The most common and mature are based on the physicochemical removal of  $CO_2$  including physical absorption (water scrubbing, organic solvent scrubbing), chemical absorption, adsorption, cryogenic separation, pressure swing adsorption (PSA), membrane technology and biological removal. In general, the methane recovery from physicochemical processes can reach >96% [36].



Graph 3-1 Global natural gas demand by region, 2008-2024. Gas demand is expected to fully recover in 2021 from its drop in 2020, although the recovery remains modest compared to the rebound after the 2008-2009 crisis [36].

#### 3.1 Absorption

Absorption processes are one of the most used technologies for natural gas purification and it is since a component of gaseous phase put in contact with a liquid phase solvent can become soluble. They can be defined also as volume processes. In general, absorption processes are carried out in a counter-current column in which gas to be separated goes in counter flow with respect to liquid absorbent and in particular, the liquid usually descends, and the gas ascends the tower. The key point lays on the fact that one of the gas components, preferably the one that must be removed, e.g., CO<sub>2</sub> presents a higher affinity with the solvent. Basing on the nature of absorbent and absorbate interaction, the absorption can be further split on physical or chemical. In physical absorption absorbent and absorbate does not react chemically but only physically that is dissolution of one gas component on the solvent. In the chemical absorption, the adsorbate reacts chemically with adsorbent or only a component. When the absorbent reach its equilibrium level, a regeneration step is needed and it is conducted by reducing partial pressure in the gas phase for physical absorption or by creating a thermal or chemical gradient in the case of chemical absorption [37], [38].

#### 3.1.1 Physical (water or organic solvent)

Physical absorption processes are those in which the solvent interact only physically with the dissolved gas and, it must have thermodynamic properties enhancing the absorption of  $CO_2$  with respect to the other gas components. This kind of processes is used when the feed gas presents a high partial pressure of  $CO_2$  but also a low temperature. Both water and solvent scrubbing relies on different solubility of  $CO_2$  and  $CH_4$  in a wash solution [39].

The wash solution can be water (water scrubbing) or organic solvent (e.g., polyethylene glycol dimethyl ether, trade name asGenosorb or Seloxol). This method involves no chemical reaction. Since the gas solubility improves with increasing pressure, pre-treated gas mixture is pressurised and injected into the scrubbing column [40].

In the water scrubbing process (Figure 3-1), the gas mixture is maintained at 6–10 bar and 40 °C. At this condition, the solubility of CO2 is approximately 26 times higher than that of  $CH_4$  [36]. The gas is injected on the bottom side of the absorption column and the water is sent in counter-current flow with respect to the gas flow in order to improve the absorption. The  $CO_2$  – water stream exiting from the bottom is sent to a flash tower that lower the pressure but also recover the remaining  $CH_4$  sending it again in the compressor inlet. Again, the  $CO_2$  – water stream is sensing on the desorption column and mixed with atmospheric air that separate the  $CO_2$  from water. The air with desorbed  $CO_2$  is sending out and also the upgraded natural 16

gas with the desired purity. The main drawback of this technology is the very amount of needed water, about 200 m<sup>3</sup>/h for a gas flow of 1000 Nm<sup>3</sup>/h [41].



Figure 3-1 Typical schematic flow sheet for water scrubbing process [40].

The organic solvent process is similar to that of water scrubbing and this based on the fact that  $CO_2$  has a higher solubility in some solvent such as Selexol or asGenosorb than in water. Consequently, a lower quantity of solvent is needed to obtain the same amount of upgraded methane and the scrubbing column can be reduced. The absorption process also occurs at lower pressure (4 to 8 bars) resulting in a lower energy demand compared to water scrubbing (6 to 10 bars).

The main drawback lays on the fact that the regeneration of organic solvent requires higher amount of energy than for water regeneration that has to be done not with depressurization as in water scrubbing but with heating steps [42], [43].

#### 3.1.2 Chemical

Chemical absorption is based on a reversible reaction between CO<sub>2</sub> with a chemical adsorbent that usually are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and other amine compounds. Their solutions have high selectivity against CO2. Amines bind with carbon dioxide to form carbonates, which can be decomposed with heating. The following reactions take place

CO<sub>2</sub>-absorption: RNH<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub> → RNH<sub>3</sub><sup>+</sup> + HCO<sub>3</sub><sup>-</sup>

CO<sub>2</sub>-desorption: RNH<sub>3</sub>+ + HCO<sub>3</sub><sup>-</sup> → RNH<sub>2</sub> + H<sub>2</sub>O + CO<sub>2</sub>

Where R is the remaining organic component and is not specific in this equation.

The chemical reaction between solvent and CO2 in the liquid phase is highly selective resulting in an extremely low absorption of CH4, and subsequently, in a high CH4 recovery of >99.95%.

A dedicated absorber column is required to wash out CO2 from the syngas stream. At the top of the absorber, a CO2 free methane is recovered. At the bottom of the column the solution with ammines and CO2 is collected and fed to the stripper unit. A cross flow recuperator and a further heating stage are used to enhance the evaporation/separation of amines from the CO2. To better strip amines off the liquid solvent air or steam are often injected in the stripper column thanks to a boiler that provides heat between 120°C and 160 °C. The heat aims to disrupt the chemical bonds formed in the absorber phase and also to create a vapor stream that acts as stripping fluid. Here, the CO2 is released to the gas phase by inverting the absorption reaction and steam is generated which lowers the CO2 partial pressure and improves desorption. Finally, a gaseous CO2 stream of high purity is collected at the head of the desorbed and the CO2-lean solvent is cooled and fed back to the absorption column. At the bottom of the stripper ammines are recovered to feed the absorber again. By increasing the pressure of the stripper, it is possible to avoid MEA and water evaporation that is very energy consuming with respect to water scrubbing regeneration.



Figure 3-2 Typical schematic flow sheet for chemical absorption process [40].

#### 3.2 Adsorption

In gas separation application, the process of adsorption is a surface process and not volumetric as in the absorption and in particular is a sort of heterogenous catalysis. This process mainly consists of the fact that some components of the gas stream (usually unwanted ones, such as  $CO_2$ ) have a higher affinity with the substrate. In particular, the substrate is a solid structure with active sites for the adsorption process. It follows that the gas stream passing through this substrate gets rid of impurities undergoing an upgrading process. Adsorption processes can be further classified into chemisorption and physisorption. In the former, chemical bonds are generated between adsorbate and substrate and the advantage is that not specific thermodynamic conditions are needed because the reaction can happen in a wide range of temperatures, but the reversible process requires a lot of energy. In the latter, there is no generation of chemical bond between adsorbate and substrate because the connection is done by means of physical forces such as electrostatic forces like Van der Walls and so, weaker compared to chemical bonds. The reversible process is easier, but some specific conditions are necessary to activate the interaction as low temperatures. Based on regeneration methods, adsorption process is most commonly divided into pressure swing adsorption (PSA), vacuum swing adsorption (VSA) and temperature swing adsorption (TSA) [35].

#### 3.2.1 Pressure and Vacuum Swing Adsorption

Pressure and vacuum swing adsorption are similar surface processes based on the principle that CH<sub>4</sub> and CO<sub>2</sub> molecules absorb in different manner in the surface of substrate. More in detail, the gas stream is fed at relatively high pressure (around 800 kPa) in the absorption column in which a molecular sieve is present, such as zeolite, activated carbon, silica gel or alumina that is able to retain CO<sub>2</sub> molecules letting pass CH<sub>4</sub> ones and the bed is loaded until saturation made from carbon dioxide molecules. After that the process goes to the next step in which the bed is depressurized releasing a  $CH_4/CO_2$  mixture with a high content of methane. The next step consists in regenerate the bed by means of depressurization in PSA o under vacuum in VSA, releasing the accumulated CO<sub>2</sub>. A further step of pressurization is applied to let methane reaching pipeline standards (Figure 3-3)[44]. Definitely, adsorption happens with gas in pressure whereas desorption under vacuum. PSA can be operated either on the basis of equilibrium or kinetic selectivity, depending on the residence time in the column. For separation based on equilibrium selectivity, the more strongly adsorbed components of a gas mixture are retained within the column, while the effluent contains the less strongly adsorbed species. In the case

of separation based on kinetic selectivity, the faster diffusing species are retained by the adsorbent and the high-pressure product is concentrated in slower diffusing components [45]. A lot of attention has to be taken to avoid methane to be released in the environment because it is a greenhouse gas twenty-one times stronger than carbon dioxide in global warming potential [42].



Figure 3-3 Typical schematic flow sheet for VSA process [40].

#### 3.2.2 Thermal Swing Adsorption

The thermal swing adsorption process differs from the pressure and vacuum ones in the regeneration mode of the substrate. In fact, it does not use pressure or vacuum but heat to get free the substrate from the carbon dioxide molecules so making it able to start again the cycle. This heat can be given directly by a heat source or also with a hot purge gas. It follows that the sweep gas for regeneration can be in small quantities with respect the other two methods. The main drawback is that it is energy-consuming method but also heat-dispending [65]. It is also used for carbon dioxide desiccation but also to remove from a gas stream very low-rate component. Very often, this method is applied for adsorbents with electrostatic charge such as zeolites that show a very high heat of adsorption, in the order of  $\Delta$ H > 30kJ/mol [51]. The waste heat depends on the reached maximum temperature but also on the concentration of gas stream to be purified.

#### 3.3 Membrane separation

Natural gas upgrading through membrane separation is one of the most recent technology basing its principle on different permeabilities of molecules. For  $CO_2/CH_4$  gas mixture separation, the carbon dioxide passes through the membrane becoming the so-called permeate whereas the methane molecules remain in the inlet side. Sometimes, the CH<sub>4</sub> molecules can pass together with carbon dioxide

stream on the permeate side, reducing the purity but also incrementing the risk of environmental damage since the methane, as previously said, is more dangerous than carbon dioxide. The membrane separation technology can be conducted in two ways: or in high pressure (usually lower than 20 bar) or at low pressure near to the atmospheric one. The degree of purity depends not only on component content in the gas stream but also in the number of stages: the higher is the times the gas is filtered the higher is the reached purity.

According to the separation media, the membrane separation process can be divided into dry gas separation, also called membrane gas separator (MGS), or wet separation as known as membrane contactor (MC) [36]. The main difference lies on the fact that in the wet mode the hydrophobic properties of micro-porous membranes are exploited and not only the selectivity as in the dry one. The polyimide and cellulose acetate membranes are able to separate  $CO_2/CH_4$  gas mixture in dry way. More in detail:

- Gas-gas separation (dry mode). The membrane gas separator membrane can be classified in three modes, according to the separation mechanism that will be mentioned in the next chapter: simple sorption diffusion, complex-sorption diffusion and electrically charged membranes [46]. The polymeric membranes with simple diffusion mechanism are the most used [47]. In this mechanism, the gas molecules in the inlet side are absorbed by the membrane then diffuses in the matrix and finally are desorbed in the permeate side. The degree of purity of the permeate product depends on the material of the membrane (Figure 3-4 (a)).
- Gas-liquid separation (wet mode). The process scheme of membrane contactor (MC) is represented in the Figure 3-4 (b) in which the porous membrane gives the mechanical support for the process, promoting the mass transfer [68]. The membrane pores are fed only with gaseous phase whereas the passage of the solvent in it has to be limited to maintain a high gas-liquid interaction at the interface of the membrane. For this reason, hydrophobic membranes are used such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polypropylene (PP). Good membrane contactors must have not only high hydrophobicity but also thermal and

chemical stability and high porosity. These characteristics are respected by polymers membranes with high melting temperatures [48].



Figure 3-4 Schematic of (a) membrane gas separation (MGS) and (b) membrane contactor (MC) for CO2 removal.

## 3.4 Cryogenic separation

The cryogenic separation is a novel method that is not as widespread as the above-mentioned ones and it is in experimental phase. It is mostly used for biogas upgrading in Netherlands and Scandinavia. Since condensation temperatures of  $CO_2$  and  $CH_4$  are very different, they can be separated by means of condensation and distillation ( $CO_2$  has a boiling point of 78°C while methane 160°C). The main requirement is that the feed gas must be in pressure around 20 bars and then lowering its temperature at around 250°C. To avoid freezing and other related problems in the cryogenic process, water,  $SO_2$  and  $H_2S$  must be previously separated. The purity of the product can be controlled by a gradual decrement of temperature [49]. Usually, the lost methane is very low by using this method and  $CO_2$  purity can reach the 98%. The main drawback is the high economic cost and the low thermal efficiency [52].

To have a general overview of the advantages and disadvantages of the technologies and make a more compact comparison, the has been elaborated.

Method	Advantages	Disadvantages
Absorption	Widely used technology for efficient (50-100) % removal of acid gases (CO2 and H2S)	Not economical as high partial pressure is needed while using physical solvents Long-time requirement for purifying acid gas as low partial pressure is needed while using chemical solvents

Absorption with	High efficiency (>97% CH4)	Expensive investment
water	Simultaneous removal of H2S when H2S (300	
Water	cm <sup>3</sup>	Clogging due to bacteria
	Easy in operation	Examing possible
	Capacity is adjustable by chapaina pressure or	Low flexibility toward variation of input
	temperature	
	Regeneration possible	903
	Tolerant for impurities	
Absorption with	High efficiency (297% CH4)	Expansive investment
	Simultaneous removal of organic S	
poryetriylerie giycor		
	Pogoporativo	
		stripping/vgeuum (boiling required)
		Reduced operation when dilution of
		alveal with water
Chemical	High efficiency (>99% CH4)	
absorption with		Heat required for regeneration
amines		
	More CO2 dissolved per unit of volume	Decomposition and poisoning of the
	(compared to water)	amines by 02 or other chemicals
	Very Iow CH4 losses (<0.1%)	Precipitation of salts
• - I 4 <sup>1</sup>		Fodming possible
Adsorption	High punity of products can be achieved	Recovery of products is lower
	Ease of adsorbent relocation to remote fields	Relatively single pure product
	when equipment size becomes a concern	
PSA/VSA	Highly efficient (95-98% CH4)	Expensive investment
Membrane	Simplicity, versatility, low capital investment	Recompression of permeate
technology	and operation	Moderate purity
	Stability at high pressure	
	High recovery of products	
	Good weight and space efficiency	
	Less environmental impact	
Gas/gas	Simple construction	Multiple steps required (modular
	Simple operation	system) to reach high purity
	High reliability	
	Small gas flows treated without proportional	
	increase of cost	
	Removal efficiency	
	<92% CH4 (1 step) or > 96% CH4	

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Gas/liquid	H2O is removed	CH4 losses
	Removal efficiency: >96% CH4	Little operational experience
	Cheap investment and operation	
	Pure CO2 can be obtained	
Cryogenic	90-98% CH4 can be reached	Expensive investment and operation
separation	CO2 and CH4 in high purity	Highly energy intensive for
	Low extra energy cost to reach liquid	regeneration
	biomethane (LBM)	Not economical to scale down to very
		small size
		Unease of operation under different
		feed stream ad it consists of highly
		integrated, enclosed system
		CO2 can remain in the CH4
Biological	Removal of H2S and CO2	Addition of H2
removal	Enrichment of CH4	Experimental - not at large scale
	No unwanted end products	

Table 3-1 Overall of natural gas purification technologies [35].

# **4** Membrane Separation Technology

Among the different technologies available to separate  $CO_2$  from natural gas, the membrane technology is that capable of being competitive as regard as cost, simplicity and compactness. Furthermore, it can be adapted in every geographic location and its modularity make it capable to be flexible as regard as the mass flow rate inlet. It is very reliable technology even if its separation efficiency is lower compared to the others present in the market [50], [51], representing its major disadvantage [52]. But considering the purification by means of amines washing they require a continue replenishing that is very energy consuming with respect the membrane solution that is environmentally friendly and with lower operational costs. They reduce the losses of methane with respect ammines absorption, and they are suitable for high flow rate of gas stream since they have a good mechanical stability. An ideal membrane for  $CO_2$  separation must have some properties [53]:

- high CO<sub>2</sub> permeability, that is the capacity of a molecule to pass through the membrane (in the next chapter more detail will be released).
- high CO<sub>2</sub>/CH<sub>4</sub> selectivity, that is the capability of membrane to select the most permeable gas and retain the other and it is usually, higher than 30.

- thermal, chemical, and structural resistance.
- plasticization resistance.
- aging resistance.
- cost-effectiveness with respect other technologies.
- ability to be cheaply manufactured into different membrane modules and easy to scale up.
- energy efficient that is having the capability of achieving separation at near-ambient conditions.

Membrane technology has gained a great consideration in NG purification recently. The number of processes and patents employing membranes for CO<sub>2</sub> removal has been growing [54].

## 4.1 Classification

As previously said, when a  $CO_2/CH_4$  gas stream is feed on membrane to be separated, it is separated due to the different partial pressures of gas components. Usually, the methane that is at high pressure remains in the inlet side of the membrane, representing the retentate whereas the carbon dioxide that passes through the membrane is called permeate and it is at low pressure. The degree of purification of the carbon dioxide stream depends on the quantity of methane molecules passing through the membrane that is a sort of undesired effect that depends on the selectivity of the membrane.

In general, literature classifies the membranes not in a unique way but in this chapter an attempt to unify the narrative existing has been made. They have been classified according their structure, geometry, separation mechanism and material.

#### 4.1.1 Structure

Basing on their structure, membranes can be solid or liquid. The former can be further subdivided in symmetric or asymmetric according to their morphology whereas the latter in supported or unsupported according to the microporous structure and thickness.



Figure 4-1 Membrane classifications according to structure or morphology.

#### 4.1.1.1 Solid membranes

a) Symmetric or isotropic membranes

*Symmetric porous membranes.* They present rigid and highly voided structure with some pores distributed in a random manner. Only the molecules with very different diameters can be effectively separated but also their must have a diameter larger than voids 'one.

*Symmetric nonporous or dense membranes.* They are characterised by a dense layer with very low number of pores so that the separation can happen only by diffusion of the components. The driving forces can be differential pressure, different concentration, or electrical gradient.

*Symmetric electrically charged membrane.* They can be both nonporous or porous but in the major cases they are microporous to give room to ions being positively or negatively charged. The separation results depend on the quantity of ions present in the membrane.

b) Asymmetric or anisotropic membranes

Anisotropic asymmetric membranes. They consist of a very dense top layer or skin and a substructure supporting it formed in a single operation or in two steps. The skin layer has a thickness of 0.1–0.5  $\mu m$  whereas the porous sublayer of about 50–150  $\mu m.$ 

Anisotropic composite membranes. They differ from the asymmetric since the layers can be made by different polymers that can be optimized independently. The top layer is the real key point for separation process as the substructure constitutes only the mechanical support.

#### 4.1.1.2 Liquid membranes

Supported liquid membranes. They have a microporous structure giving the necessary mechanical support usually made of polymers whereas the liquid-filler pores represent the selective separation barrier.

*Unsupported liquid membrane*: These are composed of thin films of liquid stabilized by a surfactant in an emulsion-type mixture [55, pag. 2].



Figure 4-2 Schematic representation of symmetric, asymmetric, and supported liquid membrane structures.

#### 4.1.2 Geometry

According to their configuration, it is possible to distinguish different types of membrane modules: plate and frame sheet membranes, spiral wound modules, tubular membranes, capillary membranes and hollow fiber membranes [56]. Plate

and frame and spiral wound belong to the planar geometry whereas tubular, hollow fiber and capillary membranes to the cylindrical one.

The desirable characteristics of a membrane configuration according to geometry are easy cleaning and maintenance, low cost, low friction to the passage of the permeate flow, uniform velocity distribution and compactness. A high degree of turbulence in the permeate side is very important to guarantee god mass transfer and lowers the fouling.



Figure 4-3 Membrane's classification according to geometry.

#### 4.1.2.1 Planar

- a) The *plate-and-frame* configuration may be square or circular, arranged in vertical or horizontal stacks and it is not able to withstand very high pressure and the surface area to volume ratio is not high. Usually, the gas feed and the permeate flow in perpendicular directions to improve the separation.
- b) In the spiral wound configuration, the sheets of membranes are 1 or 2 m long, packaged in a spiral forming a cylindrical module. and a single module may contain as many as 30 membrane envelopes. They are separated by a flexible spacer needed for the permeate flow collected on central perforated tube. With respect to the plate and frame configuration their surface area to volume ratio is high.
#### 4.1.2.2 Cylindrical

- a) The tubular membranes are characterised by modules in which the membrane casted on the inner wall of rigid porous tubes that can be made by polymer or ceramic. The various modules are then packed at the end plates inside a shell. The diameter can vary from 5 to 25 mm. Usually, the retentate flows inside the tubes whereas the permeate is collected in the end plates. Since the diameters of tubular membranes are enough large, the maintenance and cleaning are very easy with respect the following tubular membranes.
- b) Capillary membranes present inner diameter between 0.5 and 5 mm and outer diameter between 0.8 and 7 mm. The membrane itself does not need mechanical support and constitute the selective barrier. As the hollow-fiber membranes they suffer from fouling and clogging. The material most used for their fabrication is the polymeric one but inorganic capillary membranes are already present in the market[57].
- c) Hollow-fiber membranes are very fine polymeric tubes characterised by inner diameter between 0.04 and 0.05 mm and the outer diameter between 0.08 and 0.8 mm. Since the diameter is very thin, the tubes have a sufficient mechanical strength that do not require an external rigid support like the tubular ones. In particular, a very large number of hollow fibers are packed and inserted in vessels with end plates to collect the permeate. They are very compact but they are very sensible to fouling and clogging, limiting the use of different viscosity gas streams[58].

ies.	
Advantages	Disadvantages
	ies. Advantages

The Table 4-1 summarizes the advantages and disadvantages of the various membrane geometries.

module		
Plate and frame	Membrane can be easily exchanged	Exchange of membrane in the module
	Good fouling control	is labor intensive
Spiral wound	It has a good packing density	It is quite sensitive to fouling
	It has an acceptable energy consumption	
Tubular	It offers high cross-flow velocities and large pressure-drop It has a low tendency to fouling and easy to clean	It has a high operating cost

Capillary	Production cost is very low	It requires low operating pressure (up
	Membrane fouling can effectively be controlled by	to 4 bars)
	proper feed flow	
Hollow fiber	It offers high membrane area	It is difficult to control membrane
	It is a cost-effective module when compared with	fouling
	other modules	
	It can be operated at pressures in excess of 100	
	bars	

Table 4-1 Advantages and disadvantages of different membrane geometries.

#### 4.1.3 Separation mechanism

Another possible classification of membrane technology can be associated to the mechanism of gas transport through the membrane, that can vary according to the media. In the porous media, the surface selective diffusion, Knudsen diffusion and size sieving are the most involved gas transport mechanism whereas in the dense media, solution diffusion and facilitated transport are the considered ones.



Figure 4-4 Membranes classification according to separation mechanism.

#### 4.1.3.1 Porous media

Convective flow. If the pores are relatively large, from 0.1 to 10  $\mu$ m, gases permeate through the membrane and no separation occur since there is no size sieving. Hagen-Poiseuille flow. Also in this regime no gas separation occurs since the pore radius is much higher than the mean free path of the molecules and the gas diffusion occurs through molecule-molecule collisions [59]. Knudsen diffusion. In this gas transport mechanism, the pore radius (< 0.1  $\mu$ m) is of the same order of magnitude of molecules mean free path, i.e., Kn >> 1. With respect to the Hagen-Poiseuille flow, the collisions of the molecules with the pore wall are more frequent than the collisions among the molecules leading to the possibility to have gas separation. The transport rate of any gas is inversely proportional to the square root of its molecular weight. These membranes are therefore not attractive for direct gas separation applications because of the small molecular weight differences [60].

*Surface selective diffusion.* It occurs when the membrane material has a higher affinity with one of the components of a gas stream and so, the component with higher affinity will be absorbed by the membrane moving along the pore until it is desorbed to the permeate side. The component with less affinity with the membrane has lower probability to pass through it since its pores are occupied by the higher adsorbable gas. In this way, it remains in the retentate side and the gas mixture is finally separated. This type of mechanism is generally used to separate adsorbing gas with non-adsorbing gas such as CO<sub>2</sub> with He, CO<sub>2</sub> with H<sub>2</sub>. Surface diffusion generally acts in micro- and meso-porous membranes.

*Capillary condensation.* This kind of separation mechanism can happen only when partially condensed gas phase occupies a free pore. The soluble gases can permeate trough the membrane only when all the pores are filled [61].

*Size sieving.* It is the most used method for separation not only of gas stream and it is characterized by pore radius between 5 and 10 Å. The basic principle is very simple: the pores diameters are between the smaller molecules and the larger molecules of the gas stream components. The molecules with diameters lower than pores radius can pass through the membrane and arrive to the permeate side whereas the molecule with diameter higher than pore size cannot pass and remain as retentate. This mechanism applies to separating gas mixtures with very different molecular sizes such in surface selective diffusion case. Size sieving basically performs in micro-porous membrane.

#### 4.1.3.2 Dense media

Solution diffusion. The solution diffusion is one of the gas transport mechanisms used in the dense membranes, characterized by no pore channel and so, not being subjectable to the previous transport modes. The process is very similar to that of solution diffusion and consists of three steps: 1) the component with higher affinity with membrane material is absorbed occupying the pore and letting the other component at the inlet side; 2) the absorbed component diffuses along the membranes driven by different concentration between inlet and outlet side; 3) it is desorbed in the permeate side at lower pressure. This is very common in the polymeric membranes [62].



Figure 4-5 Membrane separation and gas transport mechanisms [63].

*Facilitated transport.* It is a very useful transport mechanism to overcome the low permeate flow rate in the case of solution diffusion mechanism. In particular, the facilitated transport mechanism takes the target component, in this case  $CO_2$ , combined with a facilitated transport agent and forming a temporary product FTA- $CO_2$  that can be reversible split. The product diffuse thanks the concentration gradient of this product and not only for the  $CO_2$  gradient as in the solution diffusion model. At the permeate interface, the  $CO_2$  molecule is liberated since the reverse reaction of the inlet side occurred. The FTA diffuses back to the inlet side to attach a new molecule of carbon dioxide [64].



Figure 4-6 Solution-diffusion and facilitated transport mechanism in a composite membrane. FTA represents facilitated transport agents [64].

#### 4.1.4 Material

There are three major families of membranes for NG processing, i.e., organic (polymeric) membranes, inorganic (zeolite, carbon, ceramic, metal, etc.) membranes, and mixed matrix membranes (MMMs). In the next chapter, a more detailed review will be done.

*Polymeric membranes.* They show very excellent processability but also low price and flexibility. However, polymeric membranes also exhibit low performance and tend to suffer from fouling and degradation under aggressive feed conditions limiting their future applications/development.

*Inorganic membranes.* They consist of oxides or metals and can be structured in self-supporting structures or multi-layer ones. They can be further divided into micro-porous membranes (0.5–2 nm), meso-porous membranes (2–50 nm) and macro-porous layers (>50 nm). They present higher performances with respect to polymeric membranes and can bear harsher conditions. The main drawback is the prices, that make them less competitive with respect the others [65].

*Mixed matrix membranes.* They unify the characteristic of polymeric membranes such as ease of fabrication and inorganic membranes that have higher performances by dispersing an organic filler into the polymeric matrix, becoming the most suitable candidate for natural gas purification [66]. With the quick development of nano/ synthetic technologies, many novel filler/polymer materials emerged in recent years, which gave great possibility of MMM to overcome the polymeric and inorganic membranes [67].

Table 4-2 illustrates advantages and disadvantages of the three different families of membranes.

Membranes	Advantages	Disadvantages
Polymeric	Easy synthesis and fabrication	Low chemical and thermal stability
membranes		
	Low production cost	Plasticization
	Good mechanical stability	Pore size not controllable
	Easy for upscaling and making variations in	Follows the trade-off between
	module form	permeability and selectivity
	Separation mechanism: Solution diffusion	
Inorganic	Superior chemical, mechanical, and thermal	Brittle
membranes	stability	
	Tunable pore size	Expensive
	Moderate the trade-off between permeablity and	Difficultuy in scale up
	selectivity	
	Operate at harsh conditions	
	Separation mechanism: Molecular sieving (<6A),	
	surface diffusion (<10-20 A), capillary	
	consensation (<30 A, and Knudsen	
	diffusion(<0,1um)	
Mixed matrix	Enhanced mechanical and thermal stability	Brittle at high fraction of fillers in
membranes		polymeric matrix
	Reduced plasticization	Chemical and thermal stability
		depends on the polymerci matrix
	Lower energy requirement	
	compacting at high pressure	
	Surpasses the trade-off between permeability	
	and selectivity	
	Enhanced separation performance over native	
	polymer membranes	
	Separation followed by the combined polymeric	
	and inorganic membrane principle	

Table 4-2 Advantages and disadvantages of the three families of membranes [68].

#### 4.2 Robeson upper bound

To evaluate the performances of membranes the Robeson upper bound has to be understood because it represents the limit to be overcome to reach high separation performances. The key parameters for gas separation are the permeability of a specific component of the gas mixture and the separation factor. It is known that these are trade-off parameters since the higher is the permeability of the more permeable gas component, the lower is the separation factor. This trade-off relationship elaborated by Robeson was shown to be related to an upper bound where the log of the separation factor versus the log of the higher permeability gas yielded a limit due to polymeric membranes technological limits. The upper bound relationship is expressed by:

$$P_i = k \, \alpha_{ij}^n \tag{1}$$

where  $P_i$  is the permeability of the more permeable gas,  $\alpha$  is the separation factor  $(P_i/P_j)$  and n is the slope of the log–log limit. The initial publication (1991) on the upper bound allowed for a determination of the state-of-the-art limits for polymeric gas membrane separation. With a specific goal in focus, a large number of studies have resulted with the objective to find polymeric structures which exceeded the empirical upper bound limits. It followed that a newest limit had been established in 2008 to consider these new performances. The key variables of the upper bound curves from the upper bound relationships are tabulated in Table 4-3for the present upper bound data versus the prior upper bound data for  $CO_2/CH_4$  gas pair [69].

CO2/CH4 gas pair	k	n
Prior upper bound (1991)	1073700	-2.63
Present upper bound (2008)	5369140	-2.64

Table 4-3 Tabulation of the values of the front factor k and the upper bound slope n



Graph 4-1 Robeson prior and upper bound for CO<sub>2</sub>/CH<sub>4</sub> separation (own elaboration).

The key points for the prior upper bound relationship for  $CO_2/CH_4$  separation are [70]:

Polymer	Permeability(CO2) barrers	Selectivity (CO2/CH4)
Poly (trimetylsilylpropyne)	18000	4.30
Poly (tertt-butylacetylene)	1360	8.50
Polyimide (6 FDA-ODA)	23	60.30
Polyimide (6 FDA-DAF)	32.2	51.00
Poly(methyl methacrylate)	0.65	130.00
Poly(methyl methacrylate)	0.5	140.00
Poly(tetramethyl bis L sulfone)	65	37.60

Table 4-4 Key points for determining Robeson's 1991 upper bound for CO<sub>2</sub>/CH<sub>4</sub> separation.



Graph 4-2 Key data for determination of Robeson's prior upper bound for CO<sub>2</sub>/CH<sub>4</sub> separation (own elaboration).

Experimental data points close to the present empirical upper bound for  $CO_2/CH_4$  separation are [69]:

Polymer	Permeability(CO2)	Selectivity
	barrers	(со2/сн4)
PVSH doped polyaniline	0.029	2200.00
Polypyrrole 6FDA/PMDA (25/75)-TAB	3.13	140.00
Polyimide TADATO/DSDA (1/1)-DDBT	45	60.00
Poly(diphenyl acetylene) 3°	110	47.80
Polyimide 6FDA-TMPDA/DAT (1:1)	130.2	38.90
Polyimide 6FDA-TMPDA/DAT (3:1)	187.6	33.90
Polyimide PI-5	190	33.90
Poly(diphenyl acetylene) 3e	290	31.50
Poly(diphenyl acetylene) 3f	330	27.50
Polyimide 6FDA-TMPDA	555.7	22.70
Polyimide 6FDA-durene	677.8	20.18
6FDA-based polyimide (8)	958	24.00
PIM-1	2300	18.40
PTMSP	19000	4.42
PTMSP	29000	4.46

Table 4-5 Key points for determining Robeson's 2008 upper bound for CO<sub>2</sub>/CH<sub>4</sub> separation



Graph 4-3 Data near Robeson's present upper bound for CO<sub>2</sub>/CH<sub>4</sub> separation (own elaboration).

## 5 Membrane Technology for CO<sub>2</sub> Separation from NG

### 5.1 Polymeric Membrane

The polymeric membranes are the most used for gas separation applications since they are less expensive with respect other materials but also ae easy to be produced. Even if they show a high potential for separation processes as mentioned before, their share in separation technologies is very low due to the trade-off, expressed by Robeson upper bound, between permeability and separation factor [71]. As polymeric membranes, the most used polymers are cellulose acetate (CA), cellulose triacetate (CTA), polysulfone (PSf), polydimethylsiloxane (PDMS), polymethylpentene (PMPS), polycarbonate (PC), polyimides (PI), and polyamides (PA) [72]. One important parameter of polymeric material is the glass transition temperature, T<sub>g</sub>. When the polymer is below this temperature, it is called glassy polymer whereas when it is over it is called rubbery. Glassy polymers show a rigid chain difficult to be changed in contrast with respect to polymers in rubbery state that are more flexible because plastic. In general, the glassy state can be considered as a sort of non-equilibrium state tending towards the rubbery state for the so-called "structural recovery". The transition temperature is the turning point for this changing that occur in amorphous polymers whose chain is not ordered in geometric structure even if it is solid [73].

In Figure 5-1 the temperature versus fractional free volume is represented. The free volume is the void between polymer chain allowing the gas diffuses through and it can be created by a defect in polymer packing during its formation but also by molecular chain motion on trainset state. It can be noted that polymers belonging to the glassy state with a rigid chain presents more free volume with respect those belonging to the rubbery state. In particular, the higher is the temperature the more are the number of pores and so, the admissible motion. In general, the transition from glassy state to the rubbery one is accompanied with changes on mechanical properties and heat capacity. Furthermore, it can be deduced that glassy polymers have higher solubility due to their nonequilibrium nature and so, they can be located near Robeson's upper bound.



Figure 5-1 Change in free volume for polymers in glassy and rubbery states [74].

As can be inferred, the free volume is a key parameter influencing gas transport properties and in particular, Cohen-Turnbull model expresses that the diffusion coefficients strongly increase by increasing the free volume. Fractional free volume is calculated as the difference between the experimental specific volume and the theoretical volume occupied by the polymer chains:

$$FFV = \frac{V - V_0}{V} \tag{2}$$

where V is the measured experimental specific volume of the polymer in cm<sup>3</sup>/g, and V<sub>0</sub> is the theoretical occupied volume of the polymer chains in cm<sup>3</sup>/g, calculated as the reciprocal of polymer density. Since gas solubility typically depends weakly on free volume, gas permeability coefficients often correlate well with FFV [75].

To assess the performance of polymeric membrane, the trade-off curve must be re-called. In general, this kind of membrane suffers from the inverse proportionality between selectivity and permeability: membranes with high permeability show low selectivity and vice versa. Figure 5-2 the status in terms of selectivity and permeability in polymeric membranes and the comparison of their desired performance. For example, some commercial polyimides (e.g., Matrimid 5218) display high selectivity for  $CO_2/CH_4$  but have poor performance in terms of  $CO_2$  permeation.



#### Figure 5-2

Comparison of desired selectivity and permeability in polymeric membranes by Robeson trade-off.

For a pure gas permeating through a polymer film or membrane, gas permeability,  $P_{A_r}$  is defined as:

$$P_A = \frac{N_A \cdot l}{p_2 - p_1} \tag{3}$$

where I is the membrane thickness,  $p_2$  is the upstream pressure of the membrane, and  $p_1$  is the downstream pressure normalized steady-state gas flux,  $N_A$ . Unlike flux, which depends upon I and  $\Delta p$ ,  $P_A$  is typically viewed, to a first approximation, as being a material property that is much less dependent than flux on membrane thickness and  $\Delta p$ . Typically, permeability coefficients are expressed in Barrer, where:

$$1 Barrer = 10^{-10} \frac{cm_{STP}^3 \cdot cm}{cm^2 \cdot s \cdot cmHg}$$
(4)

Using the solution-diffusion model, the gas permeability coefficient can be written as:

$$P_A = D_A \cdot S_A \tag{5}$$

Where  $S_A$  is the gas solubility coefficient, a thermodynamic parameter giving the quantity of the absorbed penetrant under equilibrium condition by the membrane.

It is expressed as the ratio of the concentration of gas in a polymer, C, to the pressure of gas, p, contiguous to the polymer:

$$S_A = \frac{c}{p} \tag{6}$$

Instead,  $D_A$  is the diffusion coefficient, a *kinetic* parameter indicating the velocity of transport of gas along the membrane. In particular, the diffusivity depends on the geometry since a molecule with large diameter slow the penetration lowering the diffusion coefficient. In some cases, it can be reverse since a big molecule can swell the membrane letting the diffusion coefficient increasing. The diffusion coefficient is expressed in cm<sup>2</sup>/sec, and solubility in cm<sup>3</sup>(STP)/(cm<sup>3</sup> polymer atm) or cm<sup>3</sup>(STP)/(cm<sup>3</sup> polymer cmHg).

Finally, another important parameter measuring the capacity of a polymer to separate two gases components (e.g., A and B) is called ideal selectivity,  $\alpha_{A/B}$ :

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{7}$$

By combining Eqs. (6), (7) selectivity can be written as:

$$\alpha_{A/B} = \frac{D_A S_A}{D_B S_B} \tag{8}$$

Like permeability, the ideal selectivity is a sort of material property of a polymer. Another measure of the ability of a membrane to separate a particular gas mixture is the separation factor,  $\alpha^*$ , where x<sub>i</sub> is the concentration of gas i in the feed and y<sub>i</sub> is the concentration of gas i in the permeate:

$$\alpha_{A/B}^* = \frac{y_A / y_B}{x_A / x_B} \tag{9}$$

This value is less frequently reported in the membrane materials literature because it depends more on operating conditions (e.g., upstream and downstream pressure and feed gas composition) than  $\alpha_{A/B}$ . Thus, the separation factor is not a material property of the polymer being used as the membrane. However, when the upstream pressure is much greater than the downstream pressure, the separation factor becomes equal to the ideal selectivity [75], that is  $\alpha_{A/B}^* = \alpha_{A/B}$ .

#### 5.1.1 Glassy polymers

Glassy polymeric membranes are the market leader for membrane gas separation since they present permeability and selectivity trade-off higher than rubbery ones. Furthermore, they are easy to reproduce but also affordable [76]. Table 5-1 shows an overview of some glassy polymers such as PSF, PES, polyetherimide (PEI), and PI resulting in high selectivity and low permeability. Their permeability tends to decrease over time since they suffer from physical aging [54] that is strongly affected by thickness of the membrane, particularly when it less than 1 micron [75]. To overcome the problem of physical aging, fillers in polymeric membranes are inserted, creating the mixed matrix membranes.

The performance of glassy polymers sometimes depends on their structure and so, the long exposition to CO<sub>2</sub> molecules can produce compaction, plasticization and swelling that decrease the performances since the morphology is changed. Plasticization occurs when the concentration of gas inside a polymer increases leading to chain motion and so, to higher fractional free volume. This, in turn, increases gas diffusion coefficients but lowers selectivity [75]. Instead, swelling is a phenomenon according to which a molecule with diameter larger than pores diameter can improve diffusion coefficients since it changes the morphology of the structure. Furthermore, in glassy polymeric membranes, the transport mechanism 42 is both size sieving since they present pores large enough to let carbon dioxide molecules to pass but also diffusion.

	Permeation temperature [°C]	CO₂permeability [barrer]	Selectivity CO2/CH4	Ref.	Year
Polyimide 6FDA-TMPDA/ DAT	35	29000	4.46	[77]	1993
PolyimidePI-5	35	8000	20	[78]	2010
Polyimide6FDA-TMPDA	25	2300	18.4	[79]	2005
Polyimide6FDA-durene	25	1100	17.7	[79]	2005
6FDA-based polyimide	25	1000	25	[78]	2010
PIM-1	25	958	24	[80]	2002
PES	35	200	5	[81]	2016
Matrimid 5218	25	187.6	33.9	[82]	2007
Matrimid 5218 + 5wt% PEG 200	35	160	9	[81]	2016
6FDA-DMN	35	7.68	34.91	[83]	2015
PES	35	1.29	46.08	[83]	2015

Table 5-1 Glassy polymer membranes.

#### 5.1.2 Rubbery polymers

The solution-diffusion model governs the transport in rubbery polymeric membranes and they tend to show high permeabilities, but low selectivities [54]. PDMS and Pebax are so far the most tested rubbery polymers for CO<sub>2</sub> separation applications. The selectivity depends on the physical interactions between gas penetrants and the polymer matrix. One of the main characteristics of rubbery membrane is the fact that they are more selective with larger and heavier molecules such as carbon dioxide ones and so their permeability performances increase by increasing the molecule size. Also, rubbery polymers membranes suffer from plasticization and swelling [84].

Table 5-2 shows some performances of membranes based on these materials, as well as other rubber polymers already used. The natural rubber shows very high permeability to carbon dioxide and moderate selectivity and it is followed by Pebax showing the same trend. Today, the enhancement on CO<sub>2</sub> permeability of this rubber polymer is carried out through the blending with additives [85].

	Permeation temperature [°C]	CO₂permeability [barrer]	Selectivity CO <sub>2</sub> /CH <sub>4</sub>	Ref.	Year
Natural rubber	25	134	34.7	[86]	1971
Pebax-1657	25	100	20	[87]	2005
Pebax	25	98	16.1	[88]	2010
Polyethylene	25	12.6	4.3	[86]	1971
Methyl rubber	25	7.5	9.5	[47]	1988
Poly(methylacrylate)	25	6.67	28.4	[47]	1988

Table 5-2 Rubbery polymer membranes.



Graph 5-1 Rubbery and glassy polymers membranes performances (own elaboration).

#### 5.2 Inorganic membranes

The inorganic membranes were birth as an alternative to overcome the main drawbacks of polymeric ones. They show higher selectivity and permeability and can withstand harsher conditions such as high temperature, high feeding pressure and treatments with aggressive liquids. Besides, since their pores are incompressible, they are not subjected to plasticization. They can be divided according to the media: porous and dense. Inorganic membranes with porous media, such as zeolites, glass, alumina, zirconia, and carbon membranes show a transport mechanism of molecular sieving and/or adsorption diffusion whereas the dense made of palladium are used for hydrogen separation [121].

One of the main drawbacks of inorganic membranes is the thickness since the selective layer is less than 5  $\mu$ m and the remaining part is mechanical support. In fact, permeation depends on thickness and too thin membranes are too weak to be handle whereas thicker membranes are more resistant but with less permeability. Very-thin self-supported membranes are fragile and so, supported ones are the preferred [85].

Membranes with pore size smaller than 2 nm are classified as microporous membrane showing high permeability with considerable selectivity and promising thermal and chemical stability. Microporous membranes can be further divided into crystalline and amorphous, according to their structure. Crystalline membranes primarily include zeolite membranes and MOF membranes, while silica membranes, carbon membranes, and other metal oxide membranes are classified as amorphous membranes [46].



Figure 5-3 Inorganic membrane classification according to the media.

#### 5.2.1 Crystalline

*Zeolite*. Zeolite membranes are composed of silicon, aluminium, and oxygen with cations such as H<sup>+</sup> or Na<sup>+</sup> and they can be found in nature or produced in synthetic way. They have a microporous structure with pore diameters ranging from 0.3 to 1.0

nm. In general, it is very difficult to obtain crack-free zeolite membranes due to the presence of defects and cracks occurring during heating. They can also contain intracrystalline defects coming from the broken of Si-O-Si bond and resulting in defects that lower the performances of this kind of membranes. Separation mechanism of zeolite membranes consists both molecular sieving and surface diffusion methods.

To change the permeance of zeolite membranes, cations must be changed according to this scheme  $K^+ < Ba^{2+} \sim Ca^{2+} < Cs^+ < Na^+$ . Table 5-3 shows the performances of commercially available zeolites membranes [85].

	Permeation temperature [°C]	CO₂ permeability [mol/m²*s*Pa]	Selectivity CO₂/CH₄	Ref.	Year
SAPO-34/alumina	27	2,4*10^-8	19	[89]	1998
SAPO-34/alpha-alumina	25	1,5*10^-7	16	[90]	2000
ΝαΥ	130	3*10^-7	6	[91]	2003
H-SAPO-34	25	0,1*10^-7	13-32	[92]	2004
DDR	28	7*10^-7	220	[93]	2004
Т	35	0,39*10^-7	400	[94]	2004
H-SAPO-34	25	0,9*10^-7	28	[95]	2005
HZSM-5	20	7,1*10^-7	65	[96]	2006
SSZ-13	25	1,7*10^-7	12	[97]	2006
Li-SAPO-34	22	1,1*10^-7	136	[98]	2007
DDR	25	3*10^-7	200	[99]	2007
DDR	30	0,55*10^-7	1000	[100]	2008
H-SAPO-34	22	18*10^-7	171	[101]	2008
Т	30	0,71*10^-7	71	[102]	2008
H-SAPO-34	25	25*10^-7	93	[103]	2009
Sil-1	23	60*10^-7	60	[104]	2011
H-SAPO-34	-	0,7*10^-7	250	[105]	2011
AIPO-18	22	6,6*10^-8	52-60	[106]	2012
SAPO34	400-500	1,2*10^-6	70	[107]	2013
AIPO-18	27-50	1,8*10^-7	31	[108]	2014
CHA-zeolite	20-200	1,5*10^-6	280	[109]	2015

SAPO-34	-	1,18*10^-6	180	[110]	2017

Table 5-3 Zeolite inorganic membranes.

#### 5.2.2 Amorphous

*Silica.* Silica membranes present a thickness between 50 and 10 nm and show very good properties from chemical and physical point of view. They are the best membranes in oxidizing and reducing environments and their permeability is greatly dependent on operating pressure [111]. Others researcher have demonstrated that the total permeance of gasses increases by increasing the temperature but the CO<sub>2</sub> permeance decreases [112]. The molecular sieving is the dominant gas transport mechanism in this kind of membranes[113]. The calcination is the most important fabrication method: they can improve their performances by increasing the calcination temperature [85]. Table 5-4 show the performances of silica membranes until now studied and the Graph 5.2 compares the performances of silica and zeolite membranes.

	Permeation temperature [°C]	CO2 permeability [mol/m²*s*Pa]	Selectivity CO₂/CH₄	Ref.	Year
Silica (TEOS)/gamma-alumina	_	3*10^-6	10	[111]	1989
Silica based (PPG)	30	1,8*10^-9	1675	[114]	1992
Silica based (PPG)	25	2*10^-8	156	[113]	1995
Silica (TEOS+MTES)/alumina	25	3,4*10^-7	71.5	[115]	1995
Silica (PTES)/alumina	30	8*10^-9	6	[116]	1997
Silica (DPDES)/alumina	30	8,1*10^-8	11	[116]	1997
Silica (TEOS)/alumina	25	2,3*10^-7	325	[112]	1998
Silica (TEOS)/alumina	100	7*10^-8	2.5	[117]	1000
Silica (TEOS)/alumina	100	8*10^-9	4.5	[117]	1999
Silica (TEOS)/alumina	35	9,2*10^-7	170	[118]	2000
Silica (ODS)/alumina	20	2*10^-8	2.1	[119]	2001
Silica (TEOS)/alumina	35	7*10^-7	80		
Silica (TEOS)/alumina	300	2*10^-7	25	[120]	2001
Silica-zirconia/alumina	35	9*10^-7	100		
Silica (TEOS-alkylamine)/alumina	60	1,3*10^-7	140	[121]	2015

Table 5-4. Silica inorganic membranes.



Graph 5-2 Zeolite and Silica inorganic membranes performances (own elaboration).

Carbon. Carbon membranes could surpass the Robeson upper bound due to their high permeability and selectivity [155]. They exhibit high thermal and chemical stability and can work in harsh environments, showing great performances compared to polymeric membranes. Li et al. have found that the ultra-micropore structure of the membrane that is comparable with the permeating molecule dimension is the key point in achieving high performances as regard as selectivity. If separation of  $CO_2/CH_4$  mixture must be performed with carbon membranes, the most suitable pore size is in the order nanometre, even if the separation of the two components lower increasing the temperature. Moreover, the chemical resistance of carbon membrane is fundamental to avoid CO<sub>2</sub> plasticization. Besides, the molecular sieving mechanism occurred due to their dissimilar molecular kinetic diameters by means of CO<sub>2</sub> with 3.30 Å and CH<sub>4</sub> with 3.80 Å [85]. Finally, the mechanism of gas transport in carbon membranes depends on membrane pores: for macropores, viscous flow; for mesopores, Knudsen diffusion; for micropores, selective adsorption and surface diffusion and for ultra-micropores, molecular sieving. The Table 5-5 gives an overview of carbon membranes performances.

	Permeation temperature [°C]	Feed pressure [bar]	CO2 permeability [barrer]	Selectivity CO₂/CH₄	Ref.	Year
CMS-550 <sup>3</sup>	35	3.5	1250	63	[122]	2002
CMS-800 <sup>4</sup>	35	3.5	43.5	200	[122]	2003
P84 polyimide	35	20	500	89	[125]	2004
Cellulose+FeO	30	20	110	27.5	[126]	2005
Polyimide+polybenzimidazole	35	2	305.5	52.31	[107]	2000
PBI/Matrimid	35	2	36.6	131.7	[127]	2009
Poly (aryl ether ketone)+Ag	35	42	95.5	67	[128]	2010
Polyetherimide (PEI)/poly(vinylpyrrolidone)(PVP)	25	42	56.6	69	[129]	2011
Deacetilated hollow fiber carbon membrane	30	2	100	100	[130]	2011
Deacetilated hollow fiber carbon membrane	70	8	500	200	[]	
Polyetherimide+SBA-15	30	7	222.5	7.5	[131]	2011
PEI AI disk/700°C	25	2	1046	27.6	[132]	2012
PIM-6FDA-OH Dry film	35	2	556	93	[133]	2013
PIM-6FDA-OH PEI AI disk	35	42036	3500	25	[134]	2013
PIM-6FDA-OH PEI AI disk	35	11049	512	88	[104]	2010
PIM-6FDA-OH PEI AI disk	25	2	426.1	56.4	[135]	2014
PBI/Kapton (75/25)	35	44471	83.1	204	[136]	2014
PBI/Kapton (50/50)	-	-	119.2	175.2	[130]	2014
PPO AI disk/600°C	20	2	147.5	19.3	[137]	2014
Matrimid Tubular alumina/850°C	25	8	11050	87.34	[138]	2015
6FDA/1,5-ND:ODA (1:1)	35	2	45	45	[168]	2015
PEI TiN4-3-disk	25	2	72.9	87.9	[139]	2016
P84-M1	35	27.5	25000	2	[140]	2016
P84-M3 asymmetric hollow fiber PEI	35	22	45000	2	[140]	2010
OPBI-750	25	1	760	105	[141]	2017
Polyimide+MCNT	25	1	6661	41.4	[142]	2017

Table 5-5 Carbon inorganic membranes.

<sup>&</sup>lt;sup>3</sup> CMS-550: carbon molecular sieves carbonized at 550°C.

 $<sup>^4</sup>$  CMS-800: carbon molecular sieves carbonized at 800  $^\circ\text{C}.$ 

CMSMs are produced via carbonization of polymeric membranes under inert environment or vacuum at elevated temperatures. They present a unique microporous structure, which discriminates gas molecules by size and shape. Polymers suitable for CMSM should not flow before decomposing. They must have high glass transition temperature, high melting point, high yield of fixed carbon and great thermal and structural stability. Along the heat treatment, the polymeric chains decompose originating an amorphous carbon skeleton with interconnected pores [123], [124].



Graph 5-3 Carbon membranes performances (own elaboration).

## 5.3 Facilitated Transport

## 5.3.1 Supported Liquid

To understand the transport mechanism of facilitated transport membranes it is possible to return back to the previous chapter. The former CO2-FT membrane was supported liquid ones in which a liquid phase containing carriers was fixed in a polymeric media.

## 5.3.2 Amine-Based Polymeric Fixed-Site-Carrier Membranes

Since the supported liquid membranes result in a very unstable configuration, researchers have created the fixed-site carrier membranes according to which carriers are incorporated directly in the polymeric chain. In this way, a more stable mechanical structure is created but in the meanwhile the selectivity is upgraded due to this carrier. Polymers based on ammines were widely used for preparation of FSC membranes. Among them, PVAm containing the highest content of primary amine groups over any polymers has been widely studied.

### 5.3.3 Ionic Liquid-Based Membranes

lonic liquids are molten salts at ambient temperature with a wide range of viscosity that affects the absorption rate since gas diffusivity and viscosity are inversely proportional. Basing on literature, the ionic liquids are interesting absorbent of 50 carbon dioxide molecules in a gas stream. The main drawback is the cost. They can be further divided into lonic Liquid-polymer and lonic Liquid-Inorganic Particlepolymer composite membranes.

a) *IL-polymer composite membranes* combine the advantages of having more mobility chain due to ionic liquid molten salts and more fractional free volume due to polymeric material. Si, enhancing gas diffusivity and in particular, the CO<sub>2</sub> permeability. [NTf2]<sup>-</sup> anion has exhibited a strong affinity with CO<sub>2</sub> molecules and for this reason, it is widely used as ionic liquid.

Polymer	L	т [°С]	Feed pressure [bar]	CO2 permeability [barrer]	CH₄ permeability [barrer]	a CO₂/CH₄	Ref.	Year
CA	[CnPy][NTf2]	23	1	5,3-71	0,17-4,84	14-31	[140]	2016
	[EnPy][NTf2]	23	1	5,3-35,7	0,17-1,45	21-31	[143]	2016
6FDA- MDA	C 12 (DAPIM)2 [NTf 2]2	35	10 atm	3.5	-	46	[144]	2013
6FDA- TeMPD	[Bmim][NTf2]	35	76 cmHg	501	34,5	14,5	[145]	2013

Table 5-6 Ionic Liquid polymer composite membranes.

b) *Ionic Liquid-Inorganic Particle-polymer composite membranes* can be considered as a sort of mixed matrix membranes. It is well-known that the inorganic particle in a polymeric matrix improve the performance of both inorganic and polymeric membranes. The only arising difficult is the adhesion between polymer and fillers: the ionic liquids molten salts can act as wetting agent, so improving the adhesion and consequently, the gas permeability [85], [146].

Polymer	IL	Particle	τ[°C]	Feed pressure [bar]	CO2 permeabilit y [barrer]	CH₄ permeabi lity [barrer]	a CO₂/ CH₄	Ref.	Year
Poly(RTIL)	[Emim][NTf2]	SAPO-34	296 K	1-1,5 atm	892		24	[146]	2010
Poly(RTIL) vinyl	[Emim][NTf2]	SAPO-34	296 K	1-1,5 atm	527.2	21.2	24.9	[147]	2011
Poly(RTIL) styrene	[Emim][NTf2]	SAPO-34	296 K	1-1,5 atm	634.6	22.4	28.3	[147]	2011
Poly(VBim) [NTf2]	[Emim][BF4]	ZIF-8	35 °C	3,5 bar	340	20.5	16.6	[148]	2013

Poly(VBim) [NTf2]	[Emim][NTf2]	ZIF-8	35 °C	3,5 bar	693.6	57.3	14.8		
Poly(VBim) [NTf2]	[Emim][B(CN )4]	ZIF-8	35 °C	3,5 bar	1062.4	86.1	12.3		
6FDA- TeMPD	[Bmim][NTf2]	ZSM-5	35 °C	75- 77cmHg	59,7+-2	3,67+- 0,13	16,3 +- 0,1	[149]	2014
PES	[Emim][NTf2]	SAPO-34	RT	30	300 GPU	4,79 GPU	62.5 8	[150]	2014
6FDA- durene	[Emim][NTf2]	HKUST-1	20 °C	2 atm	1101.6		29.3	[151]	2016
Pebax-1657 Pebax-1657	[Emim][NTf2] [Bmim][BF4]	ZIF-8 Silver	25 °C	1 bar	104.9		34.8		
		nanopo wder	35 °C	10 bar	180		61	[152]	2017
Pebax-1657	[DnBM][CI]	ZIF-8	30 °C	2 bar	261+-7	7,25+-4,1	36+ -1,7	[153]	2017
Pebax-1657	[Bmim][NTf2]	ZIF-8	23 °C	1 bar	231.4	15.98	14.4 8	[154]	2017

Table 5-7 Ionic Liquid-Inorganic Particle-polymer composite membranes.



Graph 5-4 Ionic Liquid- Polymer and Ionic Liquid-Inorganic Particle-Polymer membranes performances (own elaboration).

## 5.4 Mixed Matrix

The MMM membranes are a hybrid solution to take advantage of high selectivity given by inorganic fillers incorporated in the polymeric material that gives high

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fractional free volume. The fillers can be zeolites, silicas, carbons, or metal organic framework but even if they show good performance, the bottle neck, as said before, is the adhesion between fillers and polymer but also difficulty in fabrication. The zeolitic imidazolate frameworks (ZIFs) that are a subgroup of metal organic frameworks (MOFs) are capable to increase the compatibility between filler and polymer. Among them, zeolitic imidazolate frameworks-8 (ZIF-8) has shown good performances in separating  $CO_2/CH_4$  gas mixtures[155]. They can be classified according to the nature of the filler.



Figure 5-4 Mixed Matrix Membranes classification according to filler nature.

#### 5.4.1 Carbonaceous Fillers

There are three major types of carbon-based fillers in MMMs for NG purification: CMS, graphene (GR), and CNTs.

a) The CMS exhibits high surface area and homogeneity in pore size. Its transport mechanism is based on sieving leading to higher performances with respect to the neat polymer and higher porosity. The main challenge to be overcome is that having a rigid chain, it is almost impossible to obtain a homogenous membrane, making the industrial application very challenging [68].

- b) Graphene, a two-dimensional (2D) honeycomb structure, consists of atomic layers of sp<sup>2</sup>-hybrid carbon atoms connected by  $\sigma$  and  $\pi$  bonds and it is very used since it has good mechanical stability, high aspect ratio and it can also increase the path of diffusion, lowering the mobility of polymeric chain leading to better selectivity and permeability [109].
- c) CNTs consist of sp<sup>2</sup> hexagonal carbon atoms with cylindrical shape rolled by graphene sheets. As the filler, CNTs can be mainly divided into two categories: flexible single-walled carbon nanotubes (SWCNTs) and rigid multiwalled carbon nanotubes (MWCNTs). CNTs can present extremely high permeability because of the morphological structure, high bond energy and high surface area.

Membrane	Filler	Feed pressure [bar]	т [°С]	CO2 permeability [barrer]	a CO₂/ CH₄	Ref.	Year	
PSF	-	2	25	5	3.35			
	Shirasagi MSC-3K 10%wt.			5.5	5	[156]	2009	
	Shirasagi MSC-3K 20%wt.			6	6.5	[150]	2009	
	Shirasagi MSC-3K 30%wt.			6.84	14.9			
Matrimid 5218 (PI)	-	50psia	35	10	35.3			
	CMS 800-2 17% vol			10.3	44.4			
	CMS 800-2 19% vol			10.6	46.7	[157]	2003	
	CMS 800-2 33% vol			11.5	47.5			
	CMS 800-2 36% vol			11.6	51.7			
Ultem 1000	_	50psia	35	1.45	38.8			
(polyetherimide, PE)	CMS 800-2 16% vol			2.51	42	[100]	2002	
	CMS 800-2 20% vol			2.9	48.1	[122]	2003	
	CMS 800-2 35% vol			4.48	53.7			
Pebax MH 1657	_	0.7	35	128.6	16.3			
	graphene oxide 0,99 vol%			108	16.7	[150]	2015	
	graphene oxide 2,4 vol%			53.7	18.2	[156]	2015	
	graphene oxide 3,85 vol%			38.3	18.6			
Pebax MH 1657	_	2	30	440	19	[150]	2015	
	GO 10%wt.			250	26	[159]	2015	
PTMSP – 1.3	1.3	30	2,3*10^4	2.6				
	GO 1%wt.			2,4*10^4	2.5	[160] 201	2015	
	Graphene (XT IND) 1 wt%			1,7*10^4	2.8			

	Graphene (XT M60) 1wt%			1,9*10^4	2.3		
Matrimid 5218 (PI)	GO 10%wt.	2	30	8.84	34		
	CNT+GO 2			6.46	70.3		
	CNT+GO 2+8% wt.			20.53	53.9	[101]	0015
	CNT+GO 5+5% wt.			38.07	84.6	[161]	2015
	CNT+GO 8+2% wt.			29.89	74.5		
	CNT 10% wt.			10.29	27.8		
SPEEK	-	1.5	25	15.5	26.7		
	GO 2%wt.			14.6	28.7		
	GO 4%wt.			13.8	30.5	[162]	2015
	GO 6%wt.			12.3	32.5		
	GO 8%wt.			13.9	31.5		
COC	-	1 atm	25	0.428	7.3		
	GO 0,5%wt.			0.425	7.9		
	GO 1%wt.			0.422	9.1		
	GO 1,5%wt.	***		0.417	10.5	[163]	2016
	GO 2%wt.			0.41	11.1		
	GO 3%wt.			0.403	11.9		
	GO 5%wt.			0.4	12.6		
PDMS	-	10	25	3914	4.1		•••••••
	GO 0,25%wt.			2121	3.4		
	GO 0,5%wt.			5046	8.7		2016
	GO 0,75%wt.			2143	4.1		
Ultem 1000	-	10	35	2.4	25.8		
(polyethylenimine,	GO 0,25%wt.			2.7	40.9	[10.4]	
PEI)	GO 0,5%wt.			2.2	45	[164]	2014
	GO 0,75%wt.			1.9	58.4		
UDEL P-3500 (PSF)	-			3.9			
	SWCNTS 5%wt.	4 atm	35	5.12	22.9	[105]	0007
	SWCNTS 10%wt.			5.19	18.9	[165]	2007
	SWCNTS 15%wt.			4.52	18.5		
PI	-	15	25	16.83	10.9	[100]	
	MWCNTS 1%wt.			10.47	17.5	[123]	2010
	-	15	25	9.41	24.1		166] 2013
	BC-F-MWCNTs 2%wt			3.11	38.9	[166]	
	BC-F-MWCNTs 6%wt			2.2	62.9		
Polymer of	-		30	6211	15.5		<u>-</u>
intrinsic microporosity	SWCNTs 1%wt			1521	8.6	[10-]	_1
(PIM)	MWCNTs 1%wt			6219	8.2	[167]	2013
	PEG-f-MWCNTs 0,5%wt			7535	10.8		

	PEG-f-MWCNTs 1%wt			7813	91.9		
	PEG-f-MWCNTs 2%wt	•		12274	8.28		
	PEG-f-MWCNTs 3%wt			4816	16.3		
Pebax MH 1657	_	0,7 Mpa	35	135	15		
	MWCNTs-NH2 9%wt.			200	13	[=1]	2014
	MWCNTs-NH2 23%wt.	·		300	17	[51]	2014
	MWCNTs-NH2 33%wt.	•		360	24		
Pebax MH 1657	MWCNTs-NH2 5%wt.	2	25	87	19	[168]	2016
ABS	AC (Maxsorb Carbon) 2%wt	tra 2 e 8	20	4.31	26.6		
	AC (Maxsorb Carbon) 5%wt			5.43	29.7		
	AC (Maxsorb Carbon) 7%wt	•		7.96	31.8		
	AC (Maxsorb Carbon) 10%wt			10.81	34.3		2004
	AC (commercial Merk) 20%wt			7.49	28.4	[169]	
	AC (commercial Merk) 25%wt			9.82	32.5		
	AC (commercial Merk) 33%wt			13.16	41		
	AC (commercial Merk) 40%wt			20.5	50.5		
Pebax 2533	-		30	30	15.2		
	AC 50%wt.			47.8	14.9	[170]	2008
	AC 100%wt.	•		54.3	7.29		
PES	-	3	25	10.9	51.3	[171]	2011
	0,5% modified MWCNT		•	6.8	250	[1/1]	2011
Pebax 1657	-	0,7 MPa	35	130	53	[51]	2014
	33%-NH2 modified MWNTs		•	360	50	[ວາ]	2014
Pebax	-	2	30	205.5	54.5	[67] 2016	
	1%zinc modified graphene			137.9	30.6	[0/]	2010

Table 5-8 CMS, GR, CNT Mixed Matrix Membranes.

#### 5.4.2 Non-Carbonaceous Fillers

a) Zeolites exhibit 3D crystalline structure, with various channel and void volumes/cavities showing high sorption and diffusional abilities for different gas molecules. They are thermally stable and can create tortuous path for the unwanted gas component. The permselectivity of the mixed matrix membrane with zeolite filler can be tuned by varying the quantity incorporated so that, the right selection is crucial for the wanted separation efficiency.  b) MOFs show microporous crystalline structure in which the nodes consist of one or more metal ions (e.g., Al+3, Cr+3, Cu<sup>2</sup>+, or Zn<sup>2</sup>+) linked by bridge able to give the sieving mechanism and uniform pores diameter between 3–20 Å. Table 5-9 highlights some recent research works on zeolite and MOF-based MMMs for NG purification.

Membrane	Filler	Feed pressure [bar]	т [°С]	CO2 permeability [barrer]	a CO₂/CH₄	Ref.	Year
Polyurethane (PU)	-	10	25	69	5.89		-
	12% Zeolite 4A			109.4	7.38	[172]	2019
	12% Zeolite 3A			95.8	6.37	[1/2]	2010
	12% ZSM-5			119.3	6.82	•	
Polysulfone (PSF)	_	4	308 K	4.5	23		
	40% nanosized MCM-41			14.8	15	15	
	40% nanosized TMCS			7.8	23	[173]	2008
	40% nanosized APTES			7.3	28		
Polycarbonate (PC)	_	3.7	25	8.8	23.6		-
	20% Zeolite 4A+1% p-nitro aniline			4.61	51.8	[174]	2007
Polyimide (PI)/PSF	-			1.36	4.81	[176]	
50% wt.% each	10% ZSM-5			1.51	4.42	[1/5]	2011
Polyvinylalcohol/	-	10,2 atm	14				-
polyethylene glycol	58% zeolite A			111.3	31.5	[176]	2009
(PVA/PEG)	38,9% zeolite 5A			48	32.9		
Polyvinyl acetate	-			2.15	33.5	[177]	
(PVAc)	50% zeolite	4A		4.33	49.4	[[//]	2011
PES	-			2.7	31.4		-
	50% zeolite NaA	20 atm	35	1	39	[178]	2007
	50% zeolite AgA			1.1	59.6		
	50% zeolite 3A- NH2	10 atm	35	1.4 32 1.5 46 [1		•	
	50% zeolite 4A- NH2				46	[179]	2006
	50% zeolite 5A- NH2			2.5	36		
	20% zeolite beta	10 atm	35	1.63	32.6	[180]	
PSF	-	1	298 K	7.5	19.4	[181]	2001

	30% MCM-4			20.5	19.6			
	-	4	308K	4.5	25.9	[100]	2006	
	20% MCM-48			18.2	23.6	[182]	2006	
Matrimid	-	2 bar	35	8.3	36.6			
	15% NaY (pure			17 5	<b>∕</b> 13 3			
	species)			17.0	-0.0	[183]	2015	
	-			6.7	30			
	15% NaY (10/90			15.2	39.5			
	10% ZSM-5	2.5	35	9	30			
	10% Meso- ZSM-5			8.27	67.2	[184]	2008	
	10% MCM-48			9.35	33.4	[.0.]		
PES	-	1	35	2.88	29.4			
	20% SAPO-34	-		5.12	24.9	[185]	2010	
	10% HMA			1.53	37.4			
Matrimid 9725	_	9	308	5.9	31.2			
	30% NH2-UIO-66-			07.0	47.7	[186]	2015	
	ABA			37.9	47.7			
6FDA-oxydianiline	-	10	35	14.4	41.7			
(ODA)	25%MOF-199			21.8	50.7			
	25% NH2-MOF-199			26.6	52.4	[187]	2012	
	25% UIO-66			50.4	42.3			
	25% NH2-UIO-66			13.7	44.7			
Matrimid 5218	-	3	35	9.5	43.6		2010	
	50% ZIF-8			13	124.9	[100]	2010	
	38% MIL-53	3	35	51	47	[189]	2014	
	-	2	35	9	41.7	[190]	2009	
	30% MOF-5			20.2	44.7	[100]	2000	
	-			6.5	18.5			
	5% Cu3(BTC)2			7.8	21	[191]	2006	
	5% Mn (HCOO)2			6.5	16			
Polydimethylsiloxane	-			2500	3.1	[101]	2006	
(PDMS)	30% Cu3(BTC)2			2950	3.6	[131]	2000	
6FDA-ODA polyimides	25% MIL-53	10	35	20.5	44		2012	
	25% NH2-MIL-53			14	66	[152]	2012	
PSF asymmetric	-	6	30	204	21			
	6% ZIF-8			420	19 [193]	2015		
	6% IL@IF-8			312	34			
6FDA-DAM	-DAM - 10	35	315	10				
	15%MIL-53(AI)			351	12	[194]	2015	
	15% NH2-MIL-53 (AI)			288	15			
6FDA-DAM-HAB	-	10	35	46	34	[194]	2015	

	15%MIL-53(AI)			64	41		
	15% NH2-MIL-53 (AI)			44	65		
Polyvinylidene fluoride	_	6	25	0.9	21		
(PVDF)	10%MIL-53(AI)			1.6	21	[105]	2015
	10% NH2-MIL-53 (AI)			1.4	26	[100]	2010
m-PVDF	_	6	25	1.2	26		
	10%MIL-53(AI)			2.5	37	[195]	2015
	10% NH2-MIL-53 (AI)			2.2	43	[100]	
Pebax 1657	34% ZIF-7	3.75	25	41	44	[196]	2013
Matrimid	_	5	35	8	32	[107]	2015
	ZIF-8			26	53	[197]	2015
6FDA-DAM	_	2	25	390	24	[100]	2010
	15% ZIF-90			803	27	- [198]	

Table 5-9 Zeolite and MOF Mixed Matrix Membranes.



Graph 5-5 Carbonaceous and not carbonaceous fillers performances (own elaboration).

## 6 Case study: Matrimid ® 5218 versus PVDF membrane

Commercial *glassy* polymeric membrane Matrimid<sup>®</sup> 5218 polyimide (3,3',4,4'benzophenone tetracarboxylic dianhydride and diaminophenylindane)[199] was used. Before starting the experiment, since the films were obtained from solution casting technique, the membrane was subjected to drying procedure at room temperature to let the solvent evaporate for 24 h. After that, it was subjected to vacuum to ensure all solvent removal. It has been done because the pre-treatment of membrane is very useful to avoid aging and to maintain the gas transport properties constant for experimental period, according to literature. The membrane thickness is equal to 80 µm and the effective area is equal to 5,3 cm<sup>2</sup>. The working temperatures are set to 35°C and 50°C. It was cut manually to be inserted in the permeation cell. The chemical structure and the picture of that used in the laboratory are shown in

Figure 6-1.





Figure 6-1 Matrimid <sup>®</sup> 5218 chemical structure (on the left) and picture of that used in the laboratory (on the right).

The other tested membrane is the PVDF (polyvinylidene fluoride) + 10% CITR. Pure PVDF membranes are rubbery polymeric showing good thermal, chemical and mechanical properties with a flexible chain movement. They are considered as a gas barrier for most of gases, but they present an average permeability to  $CO_2$ ,  $O_2$ ,  $N_2$  and  $CH_4$ . For this reason, by incorporating fillers to PVDF material can enhance the possibility to use it for gas separation processes. The thickness of tested membrane is about 50 µm and the working temperature is set to 25°C. The chemical structure of PVDF and the picture of that used in the laboratory are shown in Figure 6-2.



Figure 6-2 PVDF chemical structure (on the left) and picture of that used in the laboratory (on the right).

# 6.1 Theoretical background: constant-volume variable-pressure method for gas permeability

As mentioned in the paragraph dealing with polymeric membrane, gas transport through a dense or nonporous polymeric film is often described by the solution–diffusion mechanism. The model assumes that the pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed only as a concentration gradient. According to Fick's first law, the mono-dimensional flux  $N_A$  of a gas A is expressed as:

$$N_A = -D\frac{dC_A}{dx} + w_A(N_A + N_P) \tag{10}$$

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 (typically imposed at zero).



Figure 6-3. Schematic representation of membrane technology for gas mixture separation

*Rubbery* polymers are in a sort of thermodynamic equilibrium liquid state and their gas sorption isotherms are typically described using Henry's law, according to:

$$C = k_D p \tag{11}$$

where  $k_D$  is the solubility coefficient.

On the other hand, *glassy* polymers are typically assumed to be in a nonequilibrium state containing both a hypothetical liquid state and a solid one. Their gas sorption isotherms are described by the dual-mode model based on Henry's dissolution law and Langmuir-type sorption. The former expresses gas dissolution in rubbery polymers and low molecular weight liquids whereas the latter is related to the sorption in porous solid where the Langmuir's holes arise from the flexible chain of glassy polymers. The model expressing the total gas concentration in a glassy polymer, according to dual-mode sorption, is:

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p}$$
(12)

where  $C_D$  is the gas concentration based on Henry's law sorption,  $C_H$  is the gas concentration based on Langmuir sorption,  $k_D$  is the Henry's law coefficient, b is the Langmuir hole affinity and  $C'_H$  is the Langmuir capacity constant  $[cm^3_{(STP)}/cm^3$  polymer]. The different sorption isotherms between the two models are reported in Figure 6-4.



Figure 6-4. Schematic representation of dual-mode sorption analysis [74].

In our laboratory, a constant-volume variable-pressure system measures permeate flux by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. The experimental procedure is detailed in the next paragraph. Thanks to this method, the tested gas permeability  $[cm^{3}_{(STP)}cm/(cm^{2} s cmHg)]$  is calculated according to:

$$P_{A} = \frac{V_{d} l}{p_{2} A R T} \left[ \left( \frac{dp_{1}}{dt} \right)_{ss} - \left( \frac{dp_{1}}{dt} \right)_{leak} \right]$$
(13)

where V<sub>d</sub> is the downstream volume (cm<sup>3</sup>), I is the film thickness (cm), p<sub>2</sub> is the upstream absolute pressure (cmHg), A is the film area available for gas transport (cm<sup>2</sup>), the gas constant R is 0.278 cmHg cm<sup>3</sup>/(cm<sup>3</sup>(sTP) K), T is absolute temperature (K) and  $\left(\frac{dp_1}{dt}\right)_{ss}$  and  $\left(\frac{dp_1}{dt}\right)_{leak}$  are the steady- state rates of pressure rise (cmHg/s) in the downstream volume at fixed upstream pressure and under vacuum, respectively. The downstream pressure must be ten times lower than the upstream pressure to maintain an effectively constant pressure difference across the membrane.

	Matrimid 5218	PVDF
<i>V<sub>d</sub></i> (cm <sup>3</sup> )	298	298
/ (cm)	0.008	0.005
A (cm²)	5.3	5.3

Table 6-1. Characterization of tested membranes.

# 6.2 Theoretical background: time lag method for constant diffusion coefficient

Since the studied membrane is a dense polymeric one, the gas transport mechanism is the solution-diffusion. As previously explained, this mechanism consists of three main steps:

- The feed gas that is at high pressure is sent to the membrane and the component with the highest affinity with the membrane material dissolves at the feed-side interface by a sorption mechanism. The non-sorptive component remains as retentate at the inlet.
- 2. Once dissolved in the surface, it diffuses through the membrane.
- 3. Reached the outlet side, the gas component desorbs, and the separation is occurred.

To calculate the amount of penetrant that has passed through the membrane in a considered time range and in a precise position, follow the Fick's second law:

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

The analytical solution of this equation is difficult to solve since it needs the initial boundary conditions, the value of diffusion coefficient that in turn, could be a 63

function of concentration. In this experiment, it has been assumed that the diffusion coefficient does not depend on concentration for sake of simplicity. Crank and Park [199] have demonstrated that this approximation is acceptable if the diffusion coefficient found is not assumed to be the average effective one. Furthermore, this assumption is also valid for low-sorbing penetrants in rubbery polymers. At time t = 0, the membrane can be considered at uniform initial concentration  $C_0$ . At t > 0, the membrane face corresponding at x = 0 is subjected at a constant concentration  $C_2$  by changing the gas pressure. The other face at x=I, where I is the thickness of the membrane, is exposed at  $C_1$ .

The analytical solution of Equation (14) with the previous considerations, is:

$$C = C_{2} + (C_{1} - C_{2}) \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_{1} \cos n\pi - C_{2}}{n} \sin\left(-\frac{Dn^{2}\pi^{2}t}{l^{2}}\right) + \frac{4C_{0}}{\pi} \sum_{m=0}^{\infty} \frac{1}{2m+1} \sin\left(\frac{(2m+1)\pi x}{l}\right) \exp\left[-\frac{D(2m+1)^{2}\pi^{2}t}{l^{2}}\right]$$
(15)

The direct measurement of penetrant concentration as function of time and position is very difficult to assess and for this reason, an easier kinetic method based on transient permeation is used. In this case, the concentrations at the time t = 0 (C<sub>0</sub>) and at x = I (C<sub>1</sub>) are zero. The gas molecules diffused on the membrane and escaping from it in the outlet side are collected on a volume of known size and so, the gas flux can be easily calculated from the amount of gas collected in it. The total amount of gas diffused across the membrane at time t, Q<sub>t</sub>, is given according to:

$$Q_{t} = \int_{0}^{t} -D\left(\frac{\partial C}{\partial x}\right)_{x=l} dt$$
  
=  $\frac{D t C_{2}}{l} - \frac{l C_{2}}{6} - \frac{2 l C_{2}}{\pi^{2}} \sum_{n=1}^{\infty} \frac{(-1)^{n}}{n^{2}} \exp\left(-\frac{D n^{2} \pi^{2} t}{l^{2}}\right)$  (16)

That becomes as follows when the gas flux reaches a steady state condition or when the time tends to infinite:
$$Q_t = D \frac{C_2}{l} \left( t - \frac{l^2}{6D} \right) \tag{17}$$

By plotting the amount of accumulated gas versus time in this transient permeation study (Figure 6–5) is possible to verify that an initial transient zone is overcome by a linear one when the steady state conditions are reached. The intercept of the linear trend of the amount of accumulated gas with the time axis is defined as time lag ( $Q_t = 0$  means  $t = \frac{l^2}{6D} = \vartheta$  at steady state). Finally, the diffusion coefficient is given by:

$$D = \frac{l^2}{6\theta} \tag{18}$$

All the above theoretical analysis based on permeation in transient condition was developed by Daynes in 1920 and it resulted in a very useful, effective, and easy way to calculate diffusivity in polymeric membranes. The most widely used method to measure the transport properties of dense polymeric membranes is the time lag method in a constant volume/pressure increase instrument. Although simple and quick, this method provides only relatively superficial, averaged data of the permeability, diffusivity, and solubility of gas or vapor species in the membrane. The present manuscript discusses a more sophisticated computational method to determine the transport properties on the basis of a fit of the entire permeation curve, including the transient period. Deviations of the experimental data from the theoretical curve could be attributed to the particular MOF structure, with cavities of different sizes. The fitting procedure revealed two different effective diffusion coefficients for the same gas in the case of methane and ethylene, due to the unusual void morphology in the MOFs. The method was furthermore applied to mixed gas permeation in an innovative constant-pressure/variable-volume setup with continuous analysis of the permeate composition by an on-line massspectrometric residual gas analyzer. This method can provide the diffusion coefficient of individual gas species in a mixture, during mixed gas permeation experiments. Such information was previously inaccessible, and it will greatly enhance insight into the mixed gas transport in polymeric or mixed matrix membranes [200].



Figure 6-5 A typical output curve of a time lag measurement performed on a constant volumevariable pressure instrument in the condition where the permeate pressure is negligible with respect to the feed pressure [200].

#### 6.3 Experimental set-up

The test bench in which diffusion coefficients have been evaluated was supplied by Physics Department of Calabria University. It is called "CO<sub>2</sub> capture system test" and the schematic of the equipment is represented in Figure 6–6. It has been designed so that different feed gases could be tested such as N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> and O<sub>2</sub>, each one on many independent lines controlled by mass flow controller.



Figure 6-6 Schematic representation of the apparatus used to perform tests.

P0 and P1 are pressure transducers for inlet gas line with full scale of 100 bar and 10 bar, respectively. P3 and P4 instead measure outlet gas line pressures with a full scale of 3 and 100 bar. The MKS controls the vacuum level.

T1 (not represented in the scheme) reveals the system temperature whereas T2 and T3, the inlet and outlet gas line ones. T4, upper side cell temperature, is measured by a strain gauge applied manually as well as T5 that is the lower side cell temperature.

QMS is a mass spectrometer used for determining the composition in the case of mixed-feeding gas.

The high vacuum pump stage is internally composed by different valves in order to prevent the damage of the turbo pump in the case that high pressure gases flow into shorting its life.

V10 is the valve letting gas going on the inlet of the climatic chamber whereas V15, V16 and V11 are used to let the permeated gas to pass to the vent valve (V17) for leaving the test bench, or to pass through the spectrometer to be analysed by means of V20 or reaching the buffer (B2) for the accumulation.

The membrane to be tested is placed on the climatic chamber in which the temperature can range from  $-20^{\circ}$ C to  $+80^{\circ}$ C. The feeding gas pressures can go from 0 to 35 bar. A software is used to manually control these two parameters.

The polymeric membrane under study is firstly cut and then placed into a metallic cell so that the system is divided into upstream (i.e., above the film) and downstream (i.e., under the film) sections. In order to prevent gas leakages and exchange between the upstream portion and the external ambient, the cell is provided with silicon or Viton O-ring and it closed by means of screws. In this way, only the permeating gas through the membrane is collected in the buffer B2. The upstream portion of the cell is dead end since the only interesting feature is the quantity of gas permeated through the membrane.



Figure 6-7. Permeation cell

Typically, the ratio of the permeate gas flowrate to feed gas flowrate (the so-called stage cut) would be 1% or less.

$$\Phi = \frac{Permeate flow}{Feed flow}$$
(19)

The polymeric film is supported on a sintered metal but the mass transfer resistance of it is negligible with respect to that of polymer to not compromise the real measurement of membrane characteristics. Furthermore, the effective area of the membrane is not that measured before inserting it on the permeation cell since its diameter has to be higher to guarantee stability on the support. But the O-ring, once the permeation cell is clamped, leaves an imprint on the film so identifying the part that is accessible for gas diffusion. In fact, once the experiment is conducted, the cell can be open, and the effective area of the membrane can be measured.

#### 6.3.1 Procedure

It is composed of different steps both for gas permeability and diffusion coefficient evaluations:

- 1. Choose the feeding gas between  $N_2$ ,  $H_2$ ,  $CH_4$ , CO,  $CO_2$  and  $O_2$ .
- 2. Set the value of gas stream: in these specific cases the maximum value has been chosen (100 mNL/min).
- 3. Wait until the desired pressure in the buffer B1 is reached.
- 4. During the charging of buffer B1, V7, V9 and V13 must be open whereas all the others closed.
- 5. When the desired pressure in the buffer B1 is reached, the valve V10 must be open to let the gas reach the membrane. It is important to ensure that the

feed pressure must be much higher than the permeate pressure to guarantee their difference constant for all test duration.

- 6. Wait until the pressures on both side of membranes remain constant (it means that the membrane reached the equilibrium).
- 7. Take the values of P3.
- 8. The pressure rise  $\left(\frac{dp_1}{dt}\right)_{ss}$  in the downstream volume  $(V_d)$ , is recorded as a function of time (the apparatus is left under vacuum for one night at the first test and every time the tested gas is changed).
- 9. Empty the line and degas the film by opening V15, V16, V17, V18, V19 and by maintaining V10 closed.
- 10. Repeat again the procedure several times.

## 7 Results

### 7.1 Diffusivity

The used gas for diffusivity evaluation is CO<sub>2</sub>. The useful recorded values by means of software are the pressure P3 (e.g., outlet gas line pressure) and the time corresponding to this recording. Also, the parameters connected to measurement instruments are logged but they are not consisting with the scope of this study. The temperature at which the experiment is conducted is the room temperature (25°C) and this value is kept under control thanks to climatic controlled chamber in which the set points can be set manually by pushing a button in the front side or remotely by a software input.

By plotting the pressure of the permeated gas on the downstream part of the cell versus the time, it will result for CO<sub>2</sub> as shown in Graph 7-1. For initial time instants, a transient behaviour is experienced. A steady-state zone represented by the linear trend follows but it is impossible to apply Daynes's theory for time lag method measurements since the passage from transient state to steady state is very difficult to distinguish.



Graph 7-1 Pressure versus time for CO<sub>2</sub> gas at 2.5 bar and 35°C for Matrimid.

According to Daynes's theory the constant diffusion coefficient for the considered gas can be found by considering only the steady state (e.g., the first linear trend, after 50 [s]). For this reason, the previous graph should be corrected by eliminating all the transient portion. It becomes as Graph 7-2 in which the equation of the linear trend should be plotted to estimate the diffusion coefficient.



Graph 7-2. Corrected graph to estimate Matrimid diffusion coefficient.

As previously said, it can be immediately seen that the transient zone and the steady state one are not observable and so, the time lag method for diffusion coefficients estimation is not applicable. This is valid also for PVDF membrane whose graphs are not reported for sake of simplicity.

#### 7.2 Permeability

For permeability assessment again CO<sub>2</sub> was used. Different feeding pressures have been tested for 35°C and 50°C and the experimental procedure is that described in paragraph 6.3.1. The results for both temperatures are listed in Table 7-1 where the permeation is expressed as:

Permeability	(20)
Permeation =	
And its unit of measurement is $\left[GPU = 10^{-6} \frac{cm^3}{cm^2 s \ cmHg}\right]$ .	

T=35°C			T=50°C		
P_feed [bar]	Permeability [barrer]	Permeation [GPU]	P_feed [bar]	Permeability [barrer]	Permeation [GPU]
2,5	551,21	6,9	3	410,03	5,13E+00
5	282,62	3,5	5	217,95	2,72E+00
7,2	201,22	2,5	7,4	135,31	1,69E+00
9,8	93,81	1,2	10	90,01	1,13E+00

Table 7-1 Experimental data for CO2 permeability evaluation at 35°C and 50°C





Graph 7-3. Experimental results for Matrimid CO2 permeability for different feeding pressures at 35°C and 50°C.

As done for diffusion coefficients evaluation to understand if the found values are consistent is necessary to compare them with literature review. Horn & Paul [201] made different tests with Matrimid membrane at 35°C and with thickness of 20  $\mu$ m. The results are shown in Graph 7-4.



Graph 7-4 Matrimid CO2 permeability by Horn&Paul.

At first glance, in our test bench by increasing the pressure the permeability decreases whereas for Horn & Paul increases. This can be explained by supposing plasticization phenomenon due to CO<sub>2</sub> particle dimension. Furthermore, the found CO<sub>2</sub> permeability is two orders of magnitude higher than literature one and so, is better to dealt with permeation as in Graph 7–5.



Graph 7-5. CO<sub>2</sub> permeation comparison between Horn&Paul data and experimental results for Matrimid

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Probably the test rig is oversized with respect to the permeability to be measured. Since from literature data, the PVDF presents higher overall permeability than Matrimid, it has been tested.  $CO_2$  and  $N_2$  have been tested both at 25°C.

	CO <sub>2</sub>	N <sub>2</sub>
P_feed	Permeability *10^5	Permeability*10^5
[bar]	[barrer]	[barrer]
1	4.1	1.1
1.5	4.3	3.5
2	4.4	3.7
2.5	4.8	4.1

Table 7-2 Experimental data for CO<sub>2</sub> and N<sub>2</sub> permeability evaluation at 25°C.

By analysing the literature data to make a comparison (pure PVDF [202], 10% PVDF+DMF [203]) the pure PVDF shows a very low permeability and for this reason it is necessary to insert some fillers. The Graph 7-6 reports the differences between experimental results and literature data. With respect to Matrimid with lower permeability than PVDF, the results are good even if the diffusion coefficient evaluations were impossible since transient state and steady state are not observable.



Graph 7-6. Comparison between experimental results and literature data for CO2 and N2 permeability in PVDF + fillers membranes.

# 8 Conclusions

The membrane technology is a promising technology for gas separation processes. Since carbon capture, utilization and storage is considered an interim solution for reaching decarbonization targets by 2050, the  $CO_2$  molecules replacement in natural gas hydrates is one valid alternative. The only drawback relies on the impurity of effluent gas stream once the  $CH_4$  has been replaced by  $CO_2$  molecules. It has to be consistent with grid injection standards and for this reason membranes seem to be the most outstanding among the different separation technologies. If the purification is good, the separated CO2 can be injected again to the sediment and so, increasing the replacement efficiency.

Since the literature review has focused attention on Matrimid membrane for natural gas separation, the present work reports the experimental results for this kind of material.

Unfortunately, the test rig has shown some problems due to oversizing for assessing membranes with low permeabilities. Furthermore, the diffusion coefficient has been impossible to measure since the passage from transient to steady state was not clear.

By testing membrane with higher permeability such as PVDF, the permeability remains in the order of magnitude of literature data, but the diffusion coefficient is again impossible to evaluate.

For this reason, a leakage evaluation test has been conducted to better understand the test rig behaviour. The results are shown in Graph 3-1 and unfortunately, the leakages are comparable with the increasing pressure in the permeate side due to gas permeation across the membrane.



Graph 8-1 Test rig leakage evaluations at 35°C.

Finally, further experiments must be conducted with different membranes to assess the performance of test rig, but it seems to work well with high permeability membranes. For this reason, the following are proposed for next tests:

Membrane	т [°С]	Feed pressure [bar]	CO₂ permeability [barrer]	a CO₂/CH₄	Ref.	Year
Polyimide PI-5	35	-	8000	20	[79]	2010
6FDA-based polyimide	25	-	1000	25	[79]	2010
CMS-550	35	3.5	1250	63	[123]	2003
P84 polyimide	35	20	500	89	[126]	2004
Matrimid Tubular alumina/850°C	25	8	11050	87.34	[139]	2015
PIM + PEG-f-MWCNTs 1%wt	30	-	7813	91.9	[168]	2013
6FDA-DAM+15% ZIF-90	25	2	803	27	[199]	2010

Table 8-1 Membrane proposals for next experiments.

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