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## Abstract

The European Union is fostering cleaner energy to make the EU a global leader in renewable energy and ensure that the target of at least 27% of renewables in the final energy consumption in the EU by 2030 is met. In this sense, the renewable gases such as biogas and hydrogen can play an important role to make the natural gas networks greener. In order to convert biogas into commercial grade fuel gas, the most important operation is the separation of CO<sub>2</sub> and CH<sub>4</sub> from biogas which is carried out by technologies based on unit operations like absorption or permeation. The most used technologies are water scrubbing, pressure swing adsorption (PSA), chemical and physical scrubbing. However, these current technologies are very energy intensive and membrane technology may offer an attractive alternative in terms of capital and operating costs. Hydrogen is considered as the most important energy vector in this century, H<sub>2</sub> does not exist naturally and it has to be produced and delivered. Building new infrastructures to transport hydrogen is expensive and not technically feasible in most cases. Nonetheless, using the existing natural gas grid to transport and store it, could make hydrogen a valid alternative; in order to recover the H<sub>2</sub> from the grid, a combination of technologies (including membranes) are necessary to achieve efficient separation of H<sub>2</sub> present at low concentration.

To achieve optimum performance for gas separation, the membranes should both have high permeance and selectivity. Carbon Molecular Sieve Membranes (CMSM) have been identified as very promising candidates for gas separation. They offer tunable pore structure for the separation targeted and high thermal and chemical stability. CMSM are produced by the carbonisation of a polymeric precursor under an inert atmosphere or vacuum. CMSM have a unique microporous structure which allows them to discriminate gas molecules by size and shape.

In this paper, the applications of CMSM in the projects BioHysis (Hybrid and flexible system for biogas upgrading for injection in natural gas grid) and HyGrid (Flexible hybrid separation system for H<sub>2</sub> recovery from natural gas grid) are presented. The CMSM prepared show better permeation properties than the state of the art and current commercial polymeric membranes.

## 1. The BioHysis project for biogas upgrading

Nowadays, in the European Union, biogas is used for the co-generation of electricity and heat. The biomethane injection into the natural gas networks is the application that presents greater efficiency in the future. The European Union is laying the groundwork for this new efficient application by means of the enactment of a new European regulation. Biogas is produced by the breakdown of organic material contained in waste, for example, from agricultural, municipal, manure and sewage by anaerobic digestion. At present, there is no the European Standard (EN 16723-1:2016) adopted so far by the member States to inject biogas in natural gas grids, for this reason, each country in the EU has its own requirements (Table 1). Spain has one of the most restrictive Norms.

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Table 1. Limits to inject biogas in natural gas grids (Marcogaz, 2006)

Parameter	Austria	France	Germany	Holland	Sweden	Switzerland		Spain
						unlimited injection	Limited injection	
Wobbe index (kWh/m <sup>3</sup> )	13.3-15.7	13.64-15.7 <sup>(1)</sup> 12.01-13 <sup>(2)</sup>	10.5- 5.7	43.6-44.41	45.5-48.5	13.3-15.7	-	13.403-16.058
Gross calorific value (kWh/m <sup>3</sup> )	10.7-12.8	10.7-12.8 <sup>(1)</sup> 9.5-10.5 <sup>(2)</sup>		31.5 MJ/m <sup>3</sup>		10.7-13.1		0.555-0.700
Relative density	0.55-0.65	0.555-0.700				0.55-0.70		
CH <sub>4</sub> (mol%)	> 96			> 85	> 97	> 96	> 50	>95
CO <sub>2</sub> (mol%)	< 3	< 2.5	< 6		< 3	< 4	< 6	<2,5
CO (mol%)		< 2						2
O <sub>2</sub> (mol%)	< 0.5	< 0.01	< 0.5	< 0.5	< 1.0	< 0.5	< 0.5	0.01*
H <sub>2</sub> (mol%)	< 4	< 6		< 5	< 0.5	< 5	< 5	5
Halogenated comp. F/Cl (mg/m <sup>3</sup> )	0	< 10/1		-/< 25				
NH <sub>3</sub>	Pure Technically			<3	<20			3
Hg (µg/m <sup>3</sup> )		1						1
Siloxanes (mg/m <sup>3</sup> )	<10							10
BTX (mg/m <sup>3</sup> )								500
S total (mg/m <sup>3</sup> )	<10	<30	<30	<45	<23	<30	<30	50
H <sub>2</sub> S (mg/m <sup>3</sup> )	< 5	< 5	< 5	< 5	<10ppm	< 5	< 5	
(H <sub>2</sub> S+COS) (mg/m <sup>3</sup> )								15
RSH (as S) (mg/m <sup>3</sup> )	< 6	< 6	< 15					17
H <sub>2</sub> O	Dew Point -8°C/40bar	Dew Point -8°C/MOP	Soil Temperature	<32 mg/m <sup>3</sup>	<32 mg/m <sup>3</sup>	<60mg/m <sup>3</sup>	<60 mg/m <sup>3</sup>	+2 °C 70 bar
HC (dew point)	0°C/OP	<-2C/1-70bar	Soil Temperature					+5 °C 70 bar
Dust	Pure Technically		no	no				Pure Technically
Microorganisms								Pure Technically

(1) (H gas)

(2) (B gas)

(\*) It will be accepted when the injection of biogas in the gas grid containing O<sub>2</sub> up to 0.3% mol. when [CO<sub>2</sub>] ≤ 2% mol. and H<sub>2</sub>O dew point ≤ 8°C and the volumetric flow rate is less than 5000m<sup>3</sup> N/h.

The composition of biogas will depend on the source from which the biogas is formed as shown in Table 2 (Coombs 1990, Swedish Gas Centre 2012). The major components of biogas are methane (45-80% vol.) and carbon dioxide (20-60% vol.) and a few other compounds. Therefore, its quality is not good enough to be used as fuel. The concentration of methane should be increased (biogas upgrading) and purified to be blended with natural gas and distributed in the gas network. The presence of other compounds instead of methane in biogas reduces the energy produced (energy value between 20-25 MJ/m<sup>3</sup> versus 33-38 MJ/m<sup>3</sup> of natural gas).

Being CO<sub>2</sub> the second component with the highest concentration in biogas, it should be removed in order to increase the energy values. The separation of CO<sub>2</sub> from biogas is carried out by technologies based on unit operations. These technologies can also remove, to some degree, minor components. In the industry, the methods for CO<sub>2</sub> separation are based on: a) Absorption: Physical (Purisol, Selexol, Rectisol), chemical (MEA, DEA, MDEA) and water scrubbing; b) Adsorption: PSA and TSA; c) membranes and d) other cryogenic and biological methods. A comparison of

technologies is shown in Table 3 (SGC, 2013). The most used technologies are water scrubbing, PSA, chemical scrubbing and membrane separation. Chemical scrubbers and membranes have increased their market share since 2008.

Table 2. Composition of biogas depending on the source\*

Gas (range in %)	Landfill	Agricultural waste	Sewage sludge	Industrial waste	Sanitary fill
CH <sub>4</sub>	45-60	50-80	50-80	50-70	45-65
CO <sub>2</sub>	40-60	30-50	20-50	30-50	34-55
H <sub>2</sub> O	-	Saturation	Saturation	Saturation	Saturation
H <sub>2</sub>	0-0.2	0-2	0-5	0-2	0-1
H <sub>2</sub> S	0-1	100-700ppm	0-1	0-8	0.5-100ppm
NH <sub>3</sub>	0.01-1	Traces	Traces	Traces	Traces
CO	0-0.2	0-1	0-1	0-1	Traces
N <sub>2</sub>	2-5	0-1	0-3	0-1	0-20
O <sub>2</sub>	0.01-1	0-1	0-1	0-1	0-5
VOCS	0.01-0.6	Traces	Traces	Traces	5 ppm

\*(Coombs 1990, Swedish Gas Centre 2012)

Table 3. Consumables for the biogas upgrading

Technologies	Water consumption m <sup>3</sup> /Nm <sup>3</sup>	Power consumption	Chemical consumption
Water scrubbing	0.00004-0.0004 0.5-5 m <sup>3</sup> /day	compressor, cooler, and feed pump 0.3 kWh/Nm <sup>3</sup> (capacity 400 Nm <sup>3</sup> /h) 0.23 kWh/Nm <sup>3</sup> (capacity 2000 Nm <sup>3</sup> /h)	Anti-foaming agents, 0.00003 kg/Nm <sup>3</sup> raw biogas
Chemical scrubbing	0.00003 m <sup>3</sup> /Nm <sup>3</sup> raw biogas	0.14 kWh/Nm <sup>3</sup> (lower part of plant) 0.12 kWh/Nm <sup>3</sup> (higher part of plant) Stripper column needs 0.55 kWh/Nm <sup>3</sup> raw biogas	Anti-foaming agents, 0.00003 kg/Nm <sup>3</sup> raw biogas, Make-up of amine, Activated carbon for removal of H <sub>2</sub> S
Physical scrubbing	0	Main energy consumers are compressor, cooler, and feed pump, this one consumes less energy	Activated carbon for removal of H <sub>2</sub> S. Water removed by increasing P and cooling
PSA	0	0.2-0.3 kWh/Nm <sup>3</sup>	Activated carbon for removal of H <sub>2</sub> S; Adsorbents
Membranes	0	0.2-0.3 kWh/Nm <sup>3</sup>	Activated carbon for removal of H <sub>2</sub> S

### 1.1. Membrane Separation to Upgrade Biogas to Biomethane and its Comparison with other Methods

Membranes used for biogas upgrading retain most of the methane while most CO<sub>2</sub> permeate through the membrane. Raw biogas is usually cleaned (removing of ammonia, siloxanes or volatile organic compounds, water and hydrogen sulfide) before biogas upgrading. Polymeric membranes are the most developed because of their low cost, high production, and versatility to be integrated in densely packaged modules. Under harsh environments of industrial streams, polymers membranes suffer from chemical and thermal stability. In addition, when exposed to CO<sub>2</sub> and/or organic vapours, they suffer plasticisation; the adsorbed gas in the membranes causes the polymer matrix to swell, thus reducing the CO<sub>2</sub> selectivity. Two parameters are used to characterise the performance of membranes: permeability and selectivity. In polymeric membranes there is a trade-off between these parameters; membranes with high permeability have low selectivity and vice-versa. Robeson reported the separation upper limit of polymer membranes for several binary mixtures of interest (Robeson 2008). The objective in the development of new membranes is to surpass that limit.

Micro-porous inorganic membranes (pores size < 2 nm) are made of silica, zeolites and carbon, and are able to surpass the Robeson limit. Carbon molecular sieves membranes (CMSM) are considered the next generation of membranes (Llosa 2016), they have unique features of high selectivity and permeability. CMSM are produced by the carbonisation of a polymeric precursor under an inert atmosphere or vacuum. CMSM have a unique microporous structure which allows them to discriminate gas molecules by size and shape (see Figure 1).

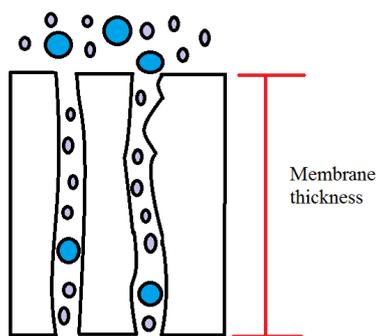


Figure 1. Transport mechanism in Carbon Molecular Sieve Membranes

In order to prepare a high performance CMSM, it is important to select an appropriate polymeric precursor and to optimise the conditions of carbonisation. New composite CMSM with improved permeation and selectivity have been developed (c-CMSM), in these membranes, inorganic nanoparticles are added to the carbon structure of the membrane. Pacheco Tanaka and Llosa Tanco reported for the first time the preparation of composite alumina-CMSM (Al-CMSM) using phenolic resins: Resol (Texeira et al., 2011, 2012), Novolac (Llosa, Pacheco et al., 2014, 2015) and composite Alumina-Ag-CMSM (Texeira et al., 2014) supported on porous alumina tubes prepared in one dip-dry-carbonisation cycle. Recently, these authors (Llosa, Pacheco, 2014) reported the influence of carbonisation temperature on pore size distribution and permeation properties of composite Al-CMSMs prepared from in house synthesised Novolac phenolic resin loaded with Boehmite nanoparticles carbonised at temperatures from 723.15 K to 1273.15 K. Micropore size distribution studies showed that the proportion of pores smaller than 0.45 nm (responsible of the sieving effect), increase as the temperature of carbonisation increases. However, the proportion of intermediate-sized micropores (0.5–0.8 nm) increase with carbonisation from 723.15 K to around 923.15 K and decrease with higher temperatures.

In the BioHysis project, supported CMSM using polyetherimide (PEI) were prepared and tested for CO<sub>2</sub> and CH<sub>4</sub> permeation. The thickness of the membrane was controlled with the concentration of the polymer in the dipping solution as it is illustrated in Figure 2a. A SEM image of the membrane prepared using 4% of polymer is shown in Figure 2b; it can be observed that a continuous defect-free CMSM of approximately 2.5 μm was formed.

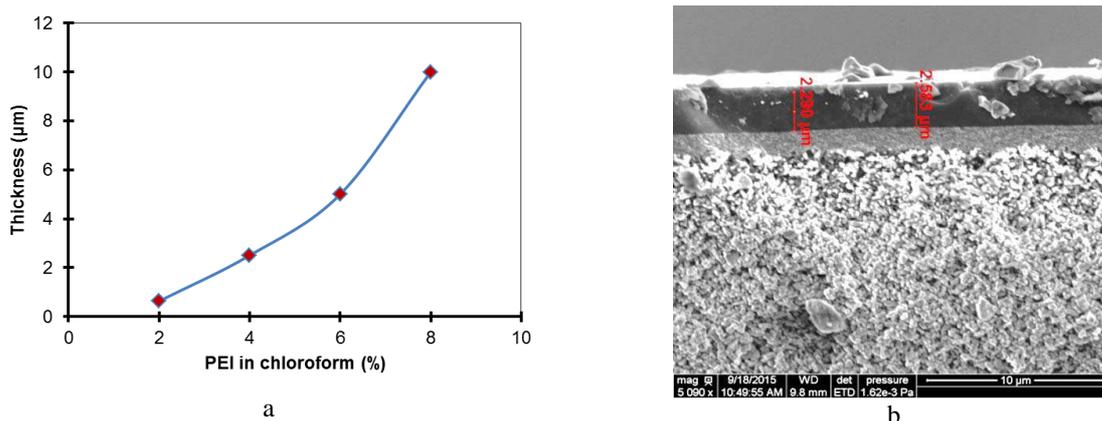


Figure 2. a) Effect of the concentration of PEI on the thickness of the membrane; b) SEM image of a CMSM prepared from a dipping solution containing 4% of PEI.

CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> permeation experiments at 35°C and 100°C at various pressure differences of a CMSM prepared from a solution containing 4% of PEI and carbonised at 550°C are presented in Figure 3 and listed in Table 4. The gas permeation increases with the pressure and CO<sub>2</sub> permeation is higher than CH<sub>4</sub> and N<sub>2</sub>. The permeation of the gases increase with the temperature and the increase is higher with CO<sub>2</sub>. In Figure 4 the permeance in function of the kinetic diameter is plotted; it can be observed that the gas permeation increase as the kinetic diameter of the gas

decrease. This is a clear indication of a molecular sieving mechanism in which gases will pass through pores that are bigger than the gas and will not do it in smaller pores. The CO<sub>2</sub> permeance is higher than expected considering only the sieving mechanism; the difference can be explained by the adsorption diffusion mechanism of CO<sub>2</sub>. In this mechanism, CO<sub>2</sub> will adsorb on the walls of the pores, and diffuses through it thanks to the gradient of concentration increasing the permeation [Llosa, Pacheco 2014]. The permeability and selectivity of the PEI membrane carbonised at 550°C were inserted in a CO<sub>2</sub>/CH<sub>4</sub> Robeson plot in Figure 5; it can be observed that the permeation of CO<sub>2</sub> carried out at 100°C is above the upper limit for polymeric membranes.

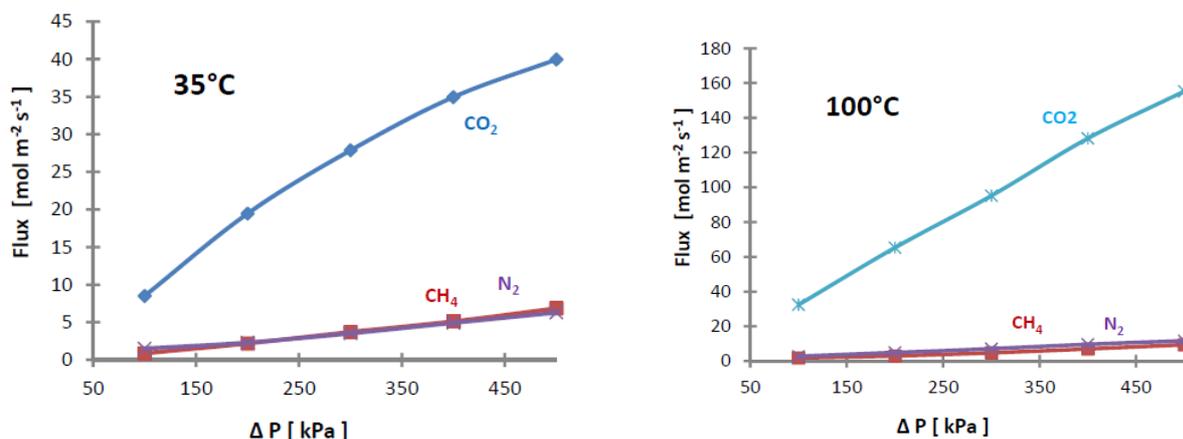


Figure 3. Gas flux of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> at 35 and 100°C at various pressures of a supported membrane prepared from a dipping solution containing 4% of PEI and carbonised at 550°C.

Table 4 - CH<sub>4</sub>, N<sub>2</sub> and CO<sub>2</sub> permeance and ideal selectivity at 35 and 100°C of a c-CMSM containing 4% of PEI carbonised at 550°C

Temperature °C	Gas permeance X10 <sup>-9</sup> mol.m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup>			Ideal selectivity CO <sub>2</sub> /CH <sub>4</sub>
	CH <sub>4</sub> (0.38 nm)*	N <sub>2</sub> (0.365 nm)*	CO <sub>2</sub> (0.33 nm)*	
35	5.2	5.6	39.2	7.5
100	7.6	10.9	123.0	16.3

\*Kinetic diameter

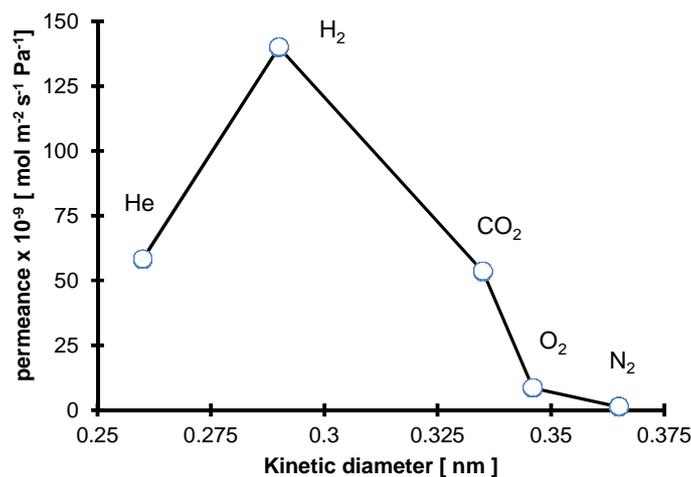


Fig 4. Permeance of alumina-CMSM carbonised at 500°C of gases with various kinetic diameters (Llosa, 2015).

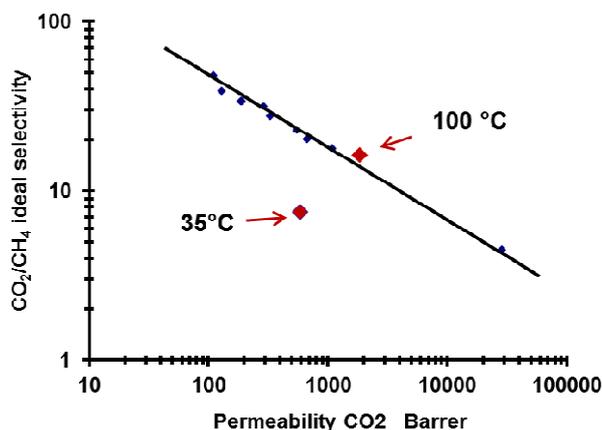


Figure 5. Robeson upper bond plot for CO<sub>2</sub>/CH<sub>4</sub> of the c-CMSM at 35°C and 100°C, containing 4% PEI carbonised at 550°C

## 2. The HyGrid project: Flexible hybrid Separation System for H<sub>2</sub> Recovery from Natural Gas Grids.

Hydrogen is considered the most important energy vector in this century and the most promising substitute of fossil fuels because of its availability and also the combustion produces only water. H<sub>2</sub> can storage high amounts of energy at a utility scale and it can be used as fuel in fuel cells for electric vehicles, in stationary fuel cells for buildings, backup power or distributed generation.

Hydrogen does not exist naturally and it has to be produced and delivered. One of the main problems for the implementation of the H<sub>2</sub> based economy is the transportation from production centres to the end users. Building new infrastructures to transport hydrogen is expensive and not technically feasible in most cases, however using the existing natural gas grid to transport and store it, could make hydrogen a valid alternative. Until 2016 there was not regulation to inject hydrogen in the natural gas grid although this parameter was considered in the norm that regulates the injection of biogas. The European Committee for Standardisation (CEN) has promoted a European Standard (EN 16726:2015) concerning the specification of gas quality of gases of group H to enhance the free flow of gas within the internal EU market. The point in using H<sub>2</sub> in the gas grid is that there is a maximum amount of H<sub>2</sub> that can be transported with the natural gas; it is in the range 2 to 10% depending on the end user's requirements. The low amounts allowed make necessary to develop technologies that are able to separate H<sub>2</sub> from main stream in a technically and affordable way.

However, cost effective separation technologies for direct separation of H<sub>2</sub> from the natural gas network should be developed for separating and purifying the H<sub>2</sub> to match the end user requirements.

The HyGrid project proposes an integral solution for developing of an advanced high performance, cost effective separation technology for direct separation of hydrogen from natural gas networks (Figure 6). The HyGrid consortium consists of 7 European organisations from 4 countries (The Netherlands, Spain, Italy and Switzerland). By using a novel membrane based hybrid technology combining three technologies integrated in a way that enhances the strengths of each of them. Membrane separation technology is employed for removing H<sub>2</sub> using water vapour as carrier gas (to increase the difference of presence in both sides of the membrane, from the “low H<sub>2</sub> content” (e.g. 2-10 %) followed by temperature swing adsorption (TSA) technology to separate water and electrochemical hydrogen separation (EHP), optimal for the “very low H<sub>2</sub> content” (e.g. <2 %). In the end, pure hydrogen will be obtained.

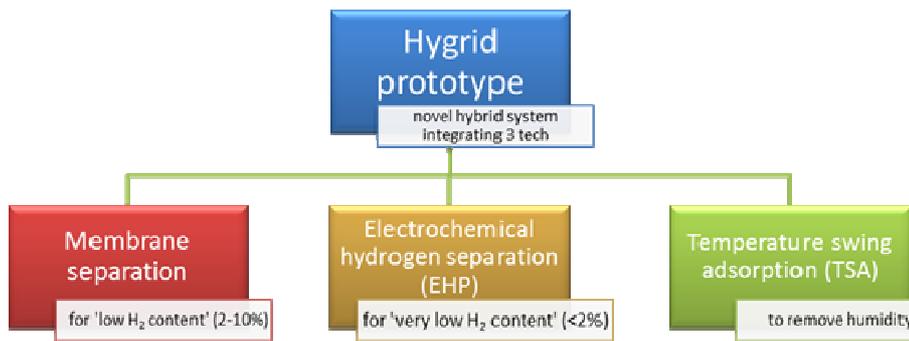


Figure 6. The HyGrid concept.

### 2.1. Membranes for hydrogen separation

Membrane separation process is a promising technology for hydrogen separation because it has a low energy requirement, low maintenance cost compared to conventional technologies and can be easily scaled-up. Several types of membranes have been developed for the purification of hydrogen; their properties are listed in Table 5.

Table 5. Properties of various hydrogen selective membranes

Properties	Polymeric membranes	Inorganic membranes*	Mixed-matrix membranes**	Pd membranes	c-CMSM
Cost	Economical to fabricate	High fabrication cost	Moderate	High fabrication cost	Moderate
Chemical stability	Moderate	High	Moderate	High	High
Mechanical Strength	Low	Excellent	Low	Excellent	Excellent
Compatibility to solvent	Limited	Wide range	Limited	Excellent	Excellent
Swelling	Frequently occurs	No	Often occurs but reduced	No	No
Separation performance	Moderate	Moderate	Above Robeson	Excellent	Above Robeson

\* Like silica sol-gel and zeolite based membranes

\*\* Polymer/inorganic-composites like zeolite or MOF filled polymer.

#### 2.1.1. Palladium based membranes

Among the membranes for hydrogen separation, CMSM and Pd membranes have the higher permeation properties; since the permeation depends on the thickness of the membrane, thin or ultra-thin membranes (< 5µm) are required. As thin membranes are mechanically weak, supported membranes are needed. In HyGrid, ultra-thin Pd-Ag and

Al-CMSM supported membranes will be developed. Dilute hydrogen poses a significant challenge for membrane technology. For example, if 10% of hydrogen is fed into a membrane separator and 70% recovery is being considered, the outlet composition of the gas would be approximately 3%. This means that to support the flux of the outlet elements of the membrane, the pressure ratio would need to be at least 33:1. So, if ambient-pressure hydrogen is recovered, the pressure of the natural gas would need to be at least 33 atm (500 psia).

Pd based membranes have very high hydrogen permeation and exclusive permeation (only hydrogen passes through the membrane) due to their unique mechanism of permeation. Among the methods to prepare thin Pd-Ag membranes, the electroless plating technique provides advantages, particularly with respect to the operational flexibility, simple equipment required, cost performance and applicability to nonconductive materials of any shape. Pacheco Tanaka and Llosa Tanco, developed a simultaneous Pd and Ag deposition method by applying a new seeding procedure (Pacheco Tanaka et al., 2005), this method allowed the control of the metal composition in the membrane and lower temperature for alloying. The addition of Ag increases the resistance to embrittlement from hydride formation of Pd at low temperature and also the hydrogen permeation reducing thus the cost. Table 6 lists the H<sub>2</sub> permeation of relevant Pd based supported membranes found in the literature.

Table 6. Hydrogen permeation properties of thin supported Pd based membranes.

Membrane	Support	Thickness μm	Technique	Temp °C	Permeance x10 <sup>-7</sup> mol m <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> at 1 atm	Selectivity H <sub>2</sub> /N <sub>2</sub>	Producer	Ref.
Pd <sub>93</sub> -Ag <sub>7</sub>	α-Al <sub>2</sub> O <sub>3</sub>	0.8	ELP	400	106	640	Tecnalia	a
Pd <sub>92</sub> -Ag <sub>8</sub>	γ-Al <sub>2</sub> O <sub>3</sub>	0.9	ELP	400	65	1100	Tecnalia	b
	Al <sub>2</sub> O <sub>3</sub> /YSZ							
Pd <sub>85</sub> -Ag <sub>15</sub>	α-Al <sub>2</sub> O <sub>3</sub>	4	ELP	400	42	20000	Tecnalia	c
Pd-Ag	α-Al <sub>2</sub> O <sub>3</sub>	2 to 10	ELP	350	6 - 31	500 to >1000	Media and process*	d
Pd	Metallic	3 to 5	ELP	450	20	450 H <sub>2</sub> /He	CRI/Criterion*	e
Pd-Ag	α-Al <sub>2</sub> O <sub>3</sub>	3 to 9	ELP	350	15	> 7600	Hysep*	f
Pd	Metallic	12	PVD- ELP	417	11	1100	Plansee/ KIT/Linde	g
Pd <sub>85</sub> -Ag <sub>15</sub>	Metallic	4-5	ELP	400	10	>200000	Tecnalia	h

\*Commercial Pd based membranes

(a) Melendez, et al., 2017

(b) Pacheco Tanaka, et al., 2015

(c) Fernandez, et al., 2014

(d) <http://www.mediaandprocess.com/products/products02.html>

(e) Ma, et al., 2014

(f) [http://www.hysep.com/fileadmin/hysep/user/documents/B-09-010\\_hysep\\_A4\\_wb.pdf](http://www.hysep.com/fileadmin/hysep/user/documents/B-09-010_hysep_A4_wb.pdf)

(g) Dittmar, et al., 2013

(h) Fernandez, et al., 2015

The objective of HyGrid is to develop of < 40 cm long supported Ultra-thin Pd/Ag membranes with H<sub>2</sub>/CH<sub>4</sub> selectivity > 10000 and hydrogen permeance > 10x10<sup>-7</sup> mol.m<sup>2</sup>s<sup>-1</sup> Pa<sup>-1</sup> at 400°C and difference in the partial pressure of H<sub>2</sub> (P<sub>H2</sub>) of 0.8 atm.

### 2.1.2. Carbon Molecular Sieve Membranes (CMSM)

CMSM have been considered as the next generation of hydrogen permeation membrane technology to work between 100 and 250°C were polymeric membranes are not stable and Pd membranes have low permeation and stability and higher cost. The H<sub>2</sub> permeance of the composite Al-CMSM from Novolac polymer loaded with Boehmite nanoparticles (Figure 4) is higher than the other gases. From N<sub>2</sub> to H<sub>2</sub>, the permeance increased as the size of the gas decreased, this is an indication of the molecular sieve mechanism separation. However, the opposite is observed between H<sub>2</sub> and He, the smaller He has lower permeation than the bigger H<sub>2</sub>. This fact is consistent with the gas transport through CMSM that combines diffusion of the permeant gases on the larger pores (Llosa, Pacheco et al. 2015). In Figure 7 (Pacheco et al., 2006), a Robeson plot of H<sub>2</sub>/N<sub>2</sub> including the permeation properties of the Al-CMSM carbonised at 550°C is shown. The novel membrane has H<sub>2</sub>/N<sub>2</sub> ideal selectivity of 725 and permeance of 1.45x10<sup>-7</sup> mol<sup>-1</sup> m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> at room temperature (Llosa, et al., 2015), these values are comparable with the best performing Pd in similar conditions. The Al-CMSM can therefore be used instead of Pd for H<sub>2</sub> separation at low temperature.

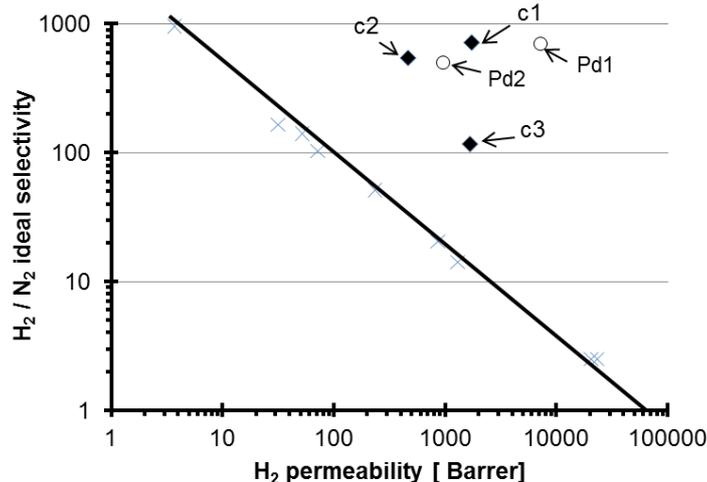


Figure 7. Robeson upper bond plot for  $H_2/N_2$  of the c-CMSM and Pd pore filled membranes, (c1) c-CMSM carbonised at  $550^\circ\text{C}$ , permeation T: $30^\circ\text{C}$ ; (c2) c-CMSM carbonised at  $600^\circ\text{C}$ , permeation T: $30^\circ\text{C}$ ; (c3) c-CMSM carbonized at  $500^\circ\text{C}$ , permeation T: $30^\circ\text{C}$  (Llosa, Pacheco, et al. 2015); (Pd1) Pd pore filling membranes at  $100^\circ\text{C}$ ; (Pd2) Pd pore filling membranes at  $50^\circ\text{C}$  (Pacheco, Llosa, et al., 2006).

At HyGrid project, three types of membranes with superior performance compared to state of the art polymeric membranes will be developed: a) Al-CMSM based on cheap polymers having moderate selectivity and low cost, b) Thin Pd/Ag membranes of 3-4  $\mu\text{m}$  on ceramic and metallic supports; these membranes will provide very high  $H_2$  selectivity and c) Ultra-thin Pd/Ag membranes ( $\approx 1 \mu\text{m}$ ) for high selectivity and very high hydrogen permeation.

### 3. Conclusions

- CMSM are versatile membranes that have higher permeation properties than polymeric membranes and are able to surpass the Robeson plot limits.
- In the BioHysis project, CMSM prepared from PEI show high permeation and selectivity towards  $\text{CO}_2$  than methane and can be used for biogas upgrading. The permeation in CMSM increases with temperature.
- In the HyGrid project, Al-CMSM and Pd/Ag silver membranes will be developed for  $H_2$  recovery from natural gas grids, promising results are being obtained.

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