tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Hydrogen purification from depleted reservoirs using membrane technology

UNDERGY Project

- **Workshop on Hydrogen Quality**
- **3rd June 2024**

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

UNDERGY H_2

UNDERGY project: Underground hydrogen storage

UNDERGY proposes to harness renewable energy by integrating renewable generation and high-capacity seasonal energy storage into a smart grid based on two levers:

- Underground seasonal storage of renewable energy, using green H_2.
- The creation of an efficient management system.

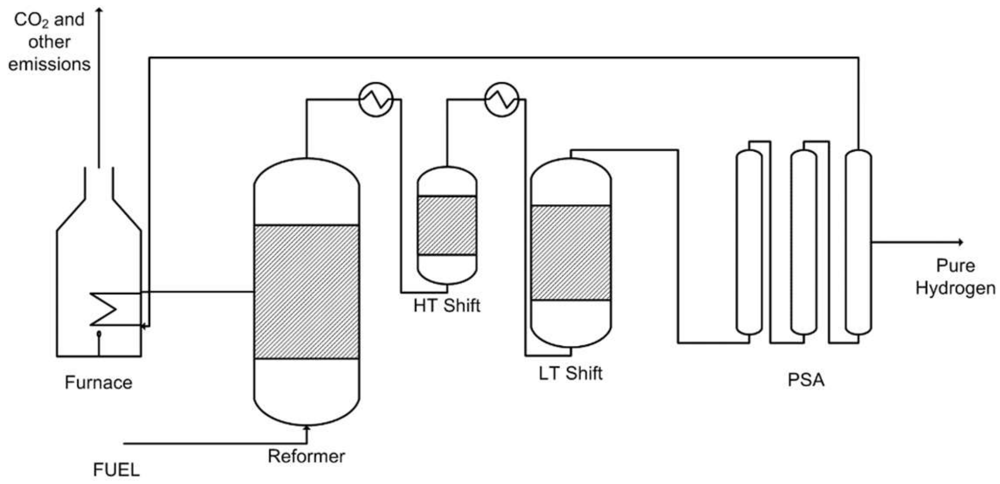
The project promotes the harness of the current national networks of gas and electricity infrastructures towards the necessary transformation into a 100% renewable distribution network.

https://undergy.eu/

- ❑ TECNALIA collaborates with TECNICAS REUNIDAS in the research of advanced membrane materials for the purification of hydrogen from streams from depleted storage (20% H_2 – 80% CH_4).
- ❑ The studies of **membrane materials** (aimed at determining the efficiency of different materials under **process conditions**), will serve for the optimization of the process and final **validation of membranes in a laboratory scale demonstrator**.

Financiado por la Unión Europea NextGenerationEU

Hydrogen Purification



Conventional process scheme for obtaining high purity hydrogen including: the conventional **steam reforming reaction**, the **high and low temperature water gas shift stages**, and the H_2 purification process by **pressure swing adsorption** (PSA)

A. Helmi, F. Gallucci, Latest Developments in Membrane (Bio)Reactors, Process. . 8 (2020). doi:10.3390/pr8101239

Technology	Advantages	Disadvantages
Pressure swing adsorption (PSA)	High capacity High purity	Unattractive for concentrations <10% of H_2 High investment cost
Cryogenic distillation	Streams with low H_2 content (<10%) can be treated Pure methane can be obtained	System complexity Extremely high energy costs High investment costs
Polymeric membranes	Low investment cost Low energy consumption Modularity Easy scalability	Limited selectivity and permeability Limited maximum purity Low thermal and chemical resistance Degradation in presence of CO_2, H_2S Unsuitable for low H_2 concentrations
CMS membranes	Low operating cost Modularity Good H_2 permeability Chemical stability in the presence of typical NG contaminants	Moderate H_2 selectivity Unattractive for concentrations < 10% H_2 Limited maximum purity Technology with limited commercial experience
Pd membranes	Low operating cost Modularity Excellent H_2 permeability Excellent selectivity	Technology with limited commercial experience Degradation in the presence of H_2S

Contaminants

Typical contaminants in the natural gas network allowed under regulations and their interaction with carbon and palladium membranes

<table>
<tr><th rowspan="2">Contaminant</th><th rowspan="2">Unit</th><th rowspan="2">Maximum quantity allowed</th><th colspan="2">Interaction of the contaminant with the membrane</th><th rowspan="2" colspan="2">Cleaning system</th></tr>
<tr><th>CMSM</th><th>Pd</th></tr>
<tr><td>S total</td><td rowspan="3">mg/m3</td><td>50</td><td rowspan="3">No</td><td rowspan="3">Yes</td><td rowspan="3" colspan="2">Activated carbon, ZnO (H_2S)
Limestone, hydrated lime, Na_2CO_3, $MgCO_3$ (SO_2)</td></tr>
<tr><td>H_2S + COS</td><td>15</td></tr>
<tr><td>RSH</td><td>17</td></tr>
<tr><td>O_2</td><td>mol%</td><td>0.01</td><td>f(T)</td><td>f(conc., T)</td><td colspan="2">-</td></tr>
<tr><td>CO_2</td><td>mol%</td><td>2.5</td><td>No</td><td>No</td><td colspan="2">Activated carbon, K_2CO_3</td></tr>
<tr><td>CO</td><td>mol%</td><td>2</td><td>No</td><td>f(T)</td><td colspan="2">Zeolite 5A</td></tr>
<tr><td>Ammonia</td><td>mg/m3</td><td>3</td><td>No</td><td>No</td><td colspan="2">Stripping + absorption</td></tr>
<tr><td>Mercury</td><td>µg/m3</td><td>1</td><td>**</td><td>**</td><td colspan="2">Activated carbon</td></tr>
<tr><td>Siloxanes</td><td>mg/m3</td><td>10</td><td>**</td><td>**</td><td>Activated carbon / silica gel, resins…</td><td rowspan="3">CLEAN-BGAS®MD DRY
(Condorchem)</td></tr>
<tr><td>BTX*</td><td>mg/m3</td><td>500</td><td>-</td><td>f(compound)</td><td></td></tr>
<tr><td>Fluor + Chlorine</td><td>mg/m3</td><td>101</td><td>**</td><td>**</td><td>$CaCl_2$ (fluor), NaOH (chlorine)</td></tr>
</table>

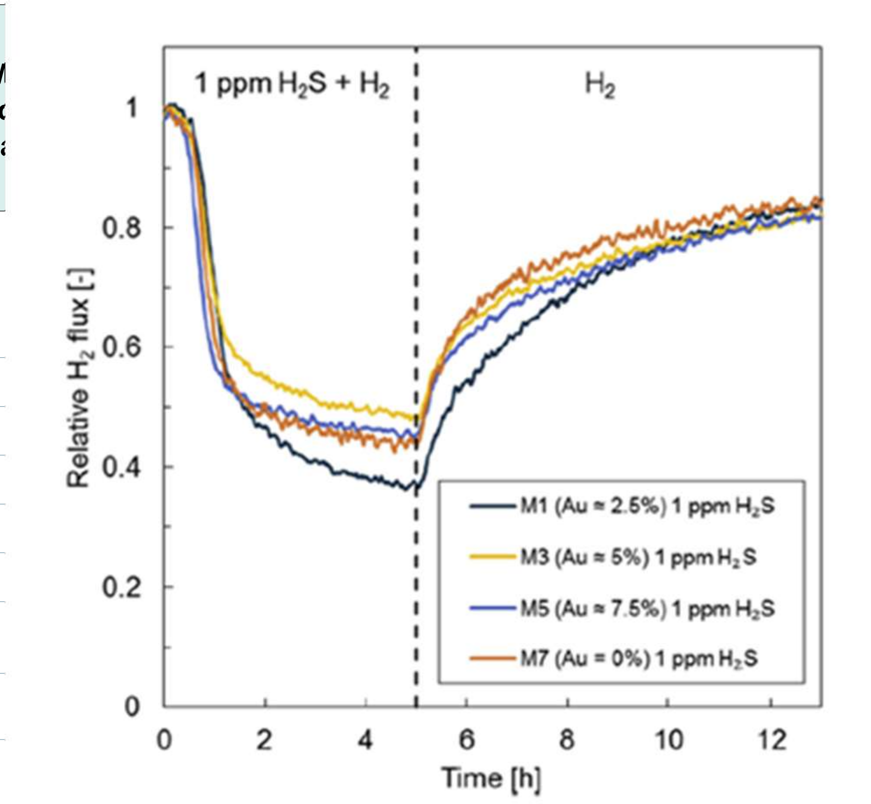
*Benzene, toluene, xylenen
** Unknown

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Contaminants

Typical contaminants in the natural gas network allowed under regulations and their interaction with carbon and palladium membranes

Contaminant	Unit	M	aning system	
S total H_2S + COS RSH	mg/m³		(H$_2$S) ne, Na_2CO_3, $MgCO_3$ (SO_2)	
O_2	mol%			
CO_2	mol%		O_3	
CO	mol%			
Ammonia	mg/m³			
Mercury	µg/m³			
Siloxanes	mg/m³		silica gel,	CLEAN-BGAS®MD DRY (Condorchem)
BTX*	mg/m³			
Fluor + Chlorine	mg/m³		hlorine)	



*Benzene, toluene, xylenen
** Unknown

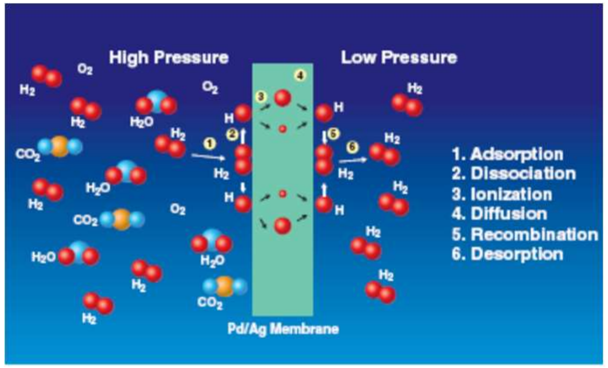
Membranes

Membrane	Thickness (μm)	T (°C)	ΔP (bar)	H_2/CH_4	Permeance H_2 (10^{-7} mol m^{-2} s^{-1} Pa^{-1})
$PdAg/Al_2O_3$	4-5	400	1	24300	11.8
DS $PdAg/Al_2O_3$	4-5	400	1	65200	13.5
$PdAg/Al_2O_3$	2-3	400	1	4280	43.6
CMSM-550	3.5	20	1	527	0.702
CMSM-600	4.2	20	1	1020	0.523

Nordio et al. International Journal of Hydrogen Energy 45 (2020) 28876-28892

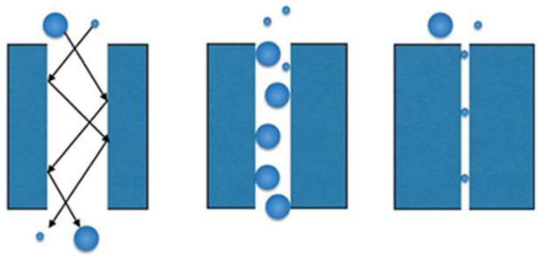
Different transport mechanisms

Pd membranes



Solution - diffusion

CMS membranes



Knudsen

Superficial

Molecular sieveing

Parameter	Pd	CMSM
Operation T(°C)	325-525	20-70
Best operation T(°C)	400-450	20-35
Maximum working pressure (bar)	80-100	
H_2 purity (vol%)*	>99.99	99.6

*Depending on H_2 concentration in feeding gas mixture, pressure and temperature conditions

Testing set up

High pressure testing set up

Pd membranes

- Pressure up to 100 bar
- Flow rate: 1 – 16 L/min

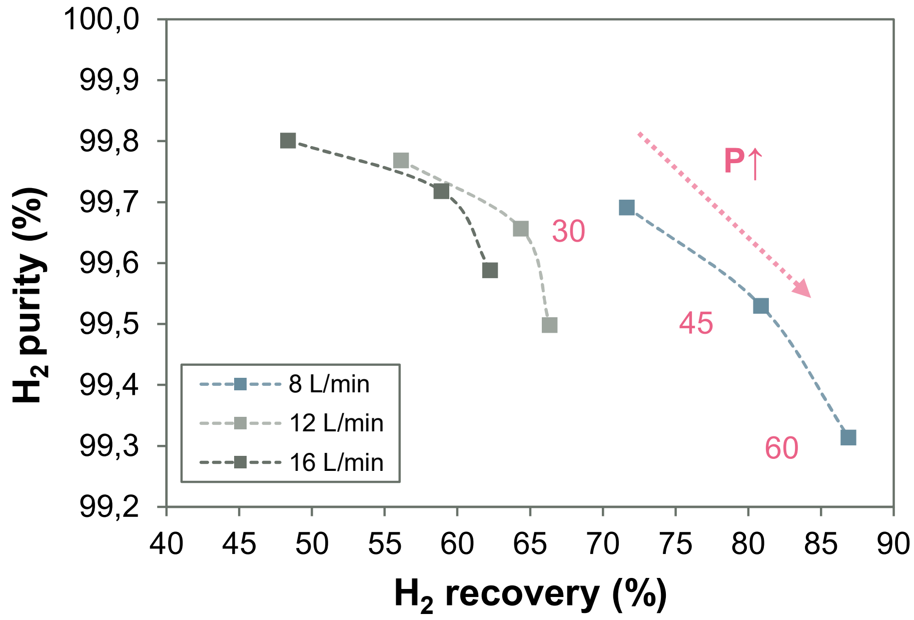
Microactivity

CMSM membranes

- Pressure up to 50 bar
- Flow rates < 1 L/min
- In a BOX Adapted to work with contaminants (H_2S, NH_3)

Pd membrane

Test parameters	
Membrane	U-PD-2B
L (mm)	130
Gas mixture	20%H_2 - 80%CH_4
ΔP (bar)	30-45-60
Feed Flow rate (L/min)	8-12-16
T (°C)	400



N_2 (400 °C & 4 barg): 5.6·10^{-11} mol m^{-2} s^{-1} Pa^{-1}

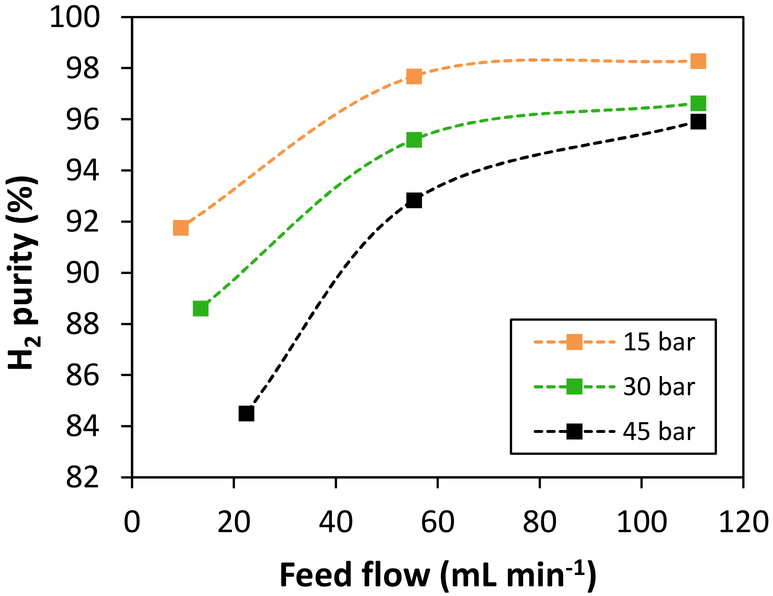
		H_2 Purity (vol.%)			H_2 recovery (vol.%)		
Membrana	Qalim (L min^{-1})	ΔP$_{mix}$ (bar)			ΔP$_{mix}$ (bar)		
		30	45	60	30	45	60
U-Pd-2A	8	99.69	99.53	99.31	71.7	80.9	86.9
	12	99.77	99.66	99.50	56.1	64.4	66.3
	16	99.80	99.72	99.59	48.3	58.9	62.2

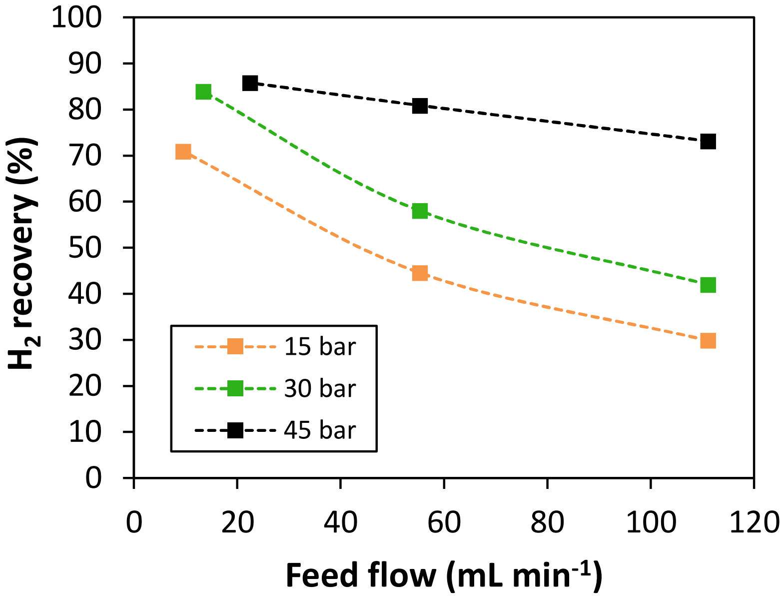
CMS membrane

Test parameters	
Membrane	CMSM-8
L (mm)	142
Gas mixture	20%H_2 - 80%CH_4 – 50 ppm H_2S
ΔP (bar)	15-30-45
Feed Flow rate (mL/min)	(9,5-22,4)* – 55,3 – 111,1
T (°C)	30

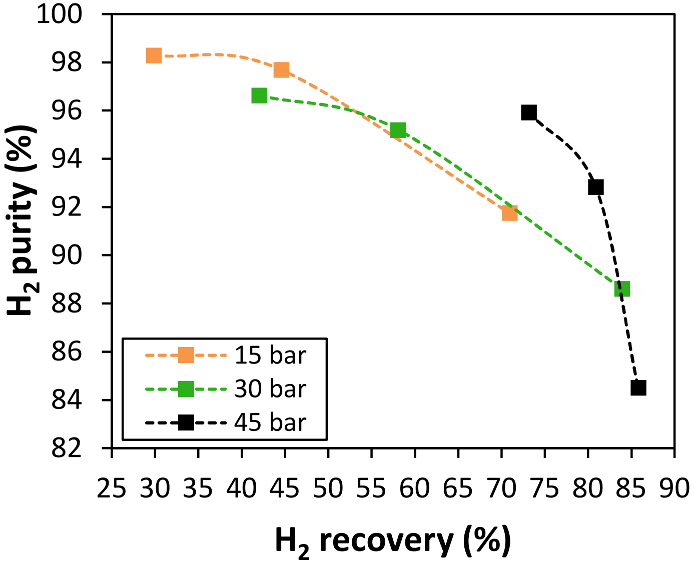
*Different depending on the pressure, in order to obtain the higher recovery %

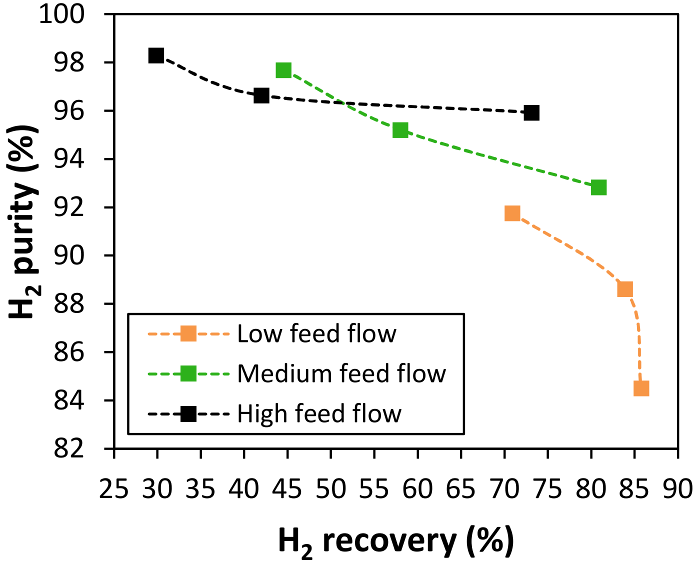
N_2 (30 °C & 5 barg): $6.5 \cdot 10^{-11}$ mol m^{-2} s^{-1} Pa^{-1}





CMS membrane





Feed flow (L min^{-1})	H_2 purity (%)			H_2 recovery (%)			H_2S perm (ppm)		
	ΔP_{mix} (bar)								
	15	30	45	15	30	45	15	30	45
9.5; 13.4; 22.4	91.8	88.6	84.5	70.9	83.9	85.8	18.6	5.0	28.7
55.3	97.7	95.2	92.8	44.5	58.0	80.9	9.7	2.0	17.3
111.1	98.3	96.6	95.9	29.8	42.0	73.1	6.2	5.0	10.3

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Main conclusions

- Using Pd membranes in H_2-CH_4 separation, H_2 purities up to 99.80% and H_2 recovery up to 86.90% can be obtained under different conditions.
- To ensure a good performance of Pd membranes, cleaning of the feeding gas mixture becomes necessary, with special attention to H_2S removal.
- Carbon molecular sieve membranes appear to be a good alternative for the purification of H_2 in the presence of H_2S.
- With CMSM, hydrogen purity and recovery can reach values of 98.3 and 85.8 respectively. Depending on the required hydrogen purity, these membranes can be used as the direct purification technique, or combined with another technique such as PSA.
- In order to further evaluate the possibility of using CMS membranes for hydrogen purification in the presence of contaminants, it is necessary to evaluate the stability of the membranes in long-term tests in the presence of H_2S as well as other contaminants.

Thank you for your attention

Jaione Ollo Loinaz
jaione.ollo@tecnalia.com
(+34) 667 10 10 62

tecnalia.com

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Financiado por la Unión Europea
NextGenerationEU