

Project no. 608535

INTERACT

INnovaTive Enzymes and polyionic-liquids based membRAnes as CO₂
Capture Technology

Deliverable 3.1:

Report on support materials performance, benchmarking tests and standardized experimental procedures of gas membrane equipment and technology

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Summary

A set of different support materials were screened and characterised. Gamma-alumina coated alfa-alumina flat sheets were found appropriate, but polymer-based supports were still selected for future work, due to their lower price and possibility to readily tune their properties. A high-throughput membrane testing system has been set-up and validated to allow future testing of the PIL-based selective layers to be developed in the frame of this project.



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1. Introduction

Ionic liquids (ILs) have emerged as unique class of versatile solvents that holds great promise for a diverse range of applications and chemical processes. These materials are considered as the next-generation solvents for CO₂ capture. Relying on their inherently low volatility and exceptional solvation capacity, intensive research efforts have been devoted to the development and engineering of suitable ILs.

ILs are solvents that consist entirely of ions and have been applied in ionic liquid-based membranes or in IL absorbers. They have a low vapor pressure along with a high chemical stability, and an intrinsic electric conductivity.² A supported ionic liquid membrane consists of a thin microporous support on which an IL is deposited. The transport mechanism of a gas through such membrane can be described by the solution–diffusion model (see also Figure 2), in which the soluble gas (e.g., CO₂) dissolves in the IL from feed side, diffuses through the IL selective layer due to a pressure gradient across the membrane and then desorbs on the permeate side at lower pressure. Only a small fraction of the gases like N₂ or CH₄ diffuses through the membrane, as it is by definition less soluble in the IL.

In this WP, IL and PIL (polymerized ILs) based membranes were prepared. In first instance, they were spincoated from solution on a porous support. The optimization of this support was the first target. Meanwhile, the high-throughput gas separation set-up (see also Figures 7 and 8) was being installed and validated to allow correct testing of the prepared membranes.



2. Support materials selection: ceramics

As support, **gamma-alumina coated alfa-alumina flat sheets** were initially selected. Their surface roughness is low enough to allow defect-free coatings with (poly-)ILs and their size was fixed to accommodate them easily in the high-throughput gas separation test equipment of KU Leuven. Typically, the IL or PIL is dissolved at a certain concentration in an organic solvent with appropriate surface tension and then spincoated. Depending on the spinning speed and the viscosity of the coating solution, a PIL or IL layer with a certain thickness after the solvent evaporation is left behind on the support. This method is more commonly known as supported IL membranes (SILMs). Part of the IL or PIL can also become immobilised in the microscopic pores through capillary force as shown in Fig. 1b (taken from Yamaguchi et al., Journal of Membrane Science, 214 (2003) 283).



Figure 1(a)

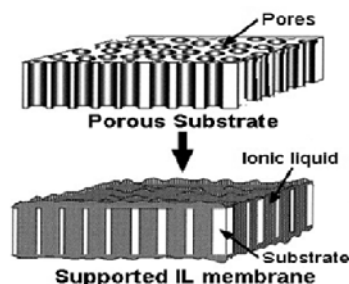


Figure 1 (b)

Gas separation with SILMs is based on the solution-diffusion mechanism, where the gas of interest dissolves in the IL, diffuses through the IL/PIL layer due to a pressure difference across the membrane, desorbs on the permeate side and is swept away by the permeate stream at low pressure (Fig. 2, taken from Hojniak et al., Journal of Physical Chemistry B, 117 (2013) 15131).

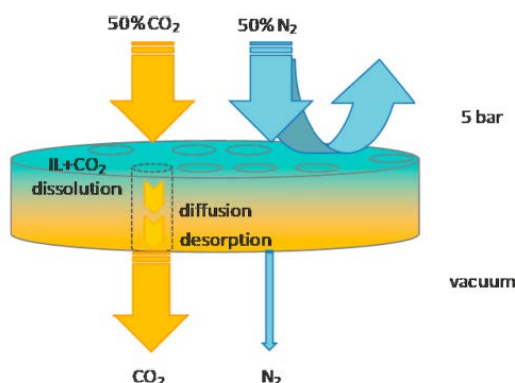


Figure 2

3. Support material selection: polymers

As a (cheaper and easier to handle) alternative to these ceramic supports, also **polymer-based supports** were developed. Surface and bulk porosity, as well as surface roughness were tuned to allow deposition of thin, defect-free selective PIL layers. Different polymer chemistries were screened for the supports. The polymers have to be stable later on when brought in contact with the coating solution, i.e. not dissolve in the solvent in which the PILs are dissolved.

3.1. Preparation of polymeric supports

For that purpose, polysulfone (PSf), polyimide (PI), polyvinylidene fluoride (PVDF) and polyacrylonitrile (PAN) supports with different structure were systematically prepared. All the supports were cast using a casting knife as shown in figure 3. Polymer layers with different thickness can be obtained by using knives with variable slit-width and by casting them at different speed. The cast film was solidified and given the appropriate porous structure via the phase inversion method by immersing it into a non-solvent coagulation bath after giving it specific time of evaporation. This support is then ready for spincoating after applying the right post treatments. The purpose of these is to prevent intrusion of the cast solution, to adjust the surface tension of the support and to prevent pore collapse during the full preparation procedure.

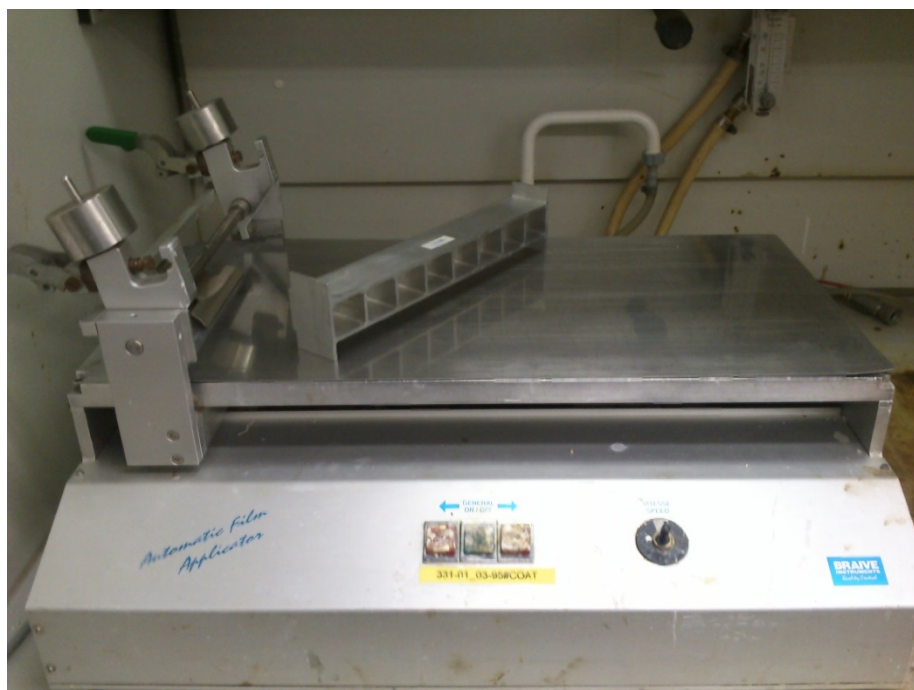


Figure 3: Automatic membrane casting device

The supports were characterized with SEM and with water permeation to define their morphology and permeability respectively. Finally, a di-amine cross-linked PI came out as the best option for further coating with PILs. These supports combined chemical and thermal stability, ease of handling, reduced surface roughness and good wettability. Preparation and performance details of the tested supports are given below.

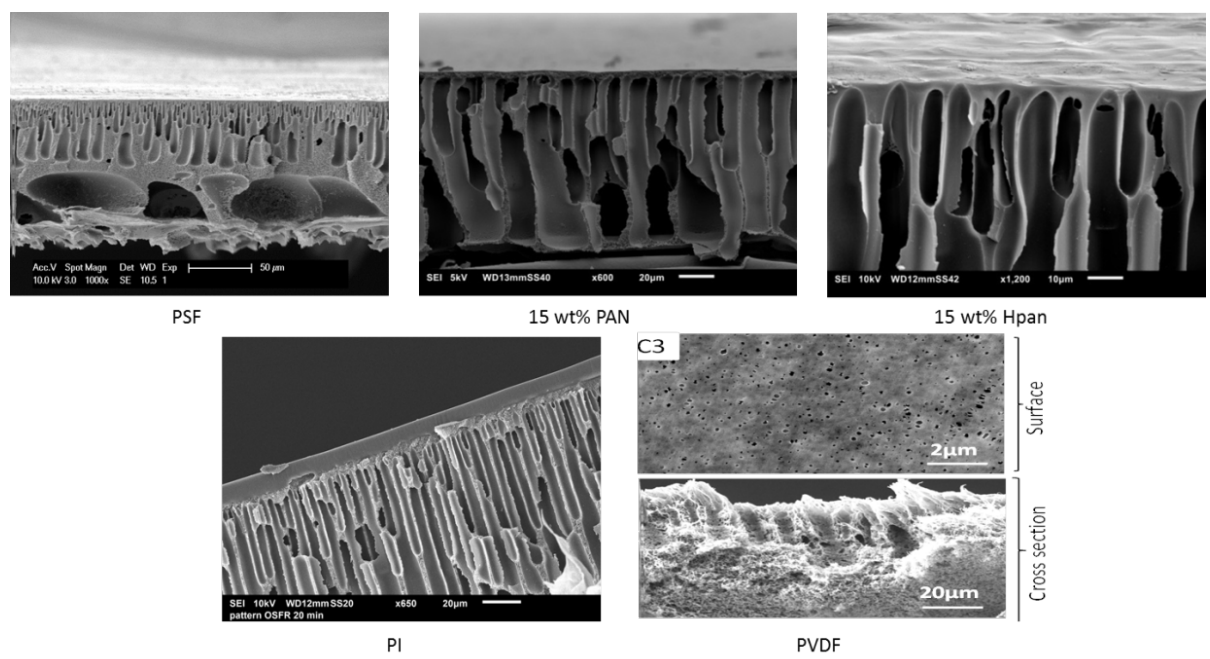


Figure 4: SEM images of synthesised support systems from different polymers

3.2. Filtration results of the support systems

3.2.1. PSf

Preparation

Polymer solution: 18 wt% PSf (Udel P-1700) in NMP

Casting thickness: 200 μm

Casting speed: position 5 (0,044 m/s)

Coagulation bath for phase inversion: distilled water

Filtration data

Feed solution: 35 μM Rose Bengal in ethanol; pressure = 1 bar

Pure water permeance = 200 – 300 $\text{L}/\text{m}^2 \text{ h bar}$

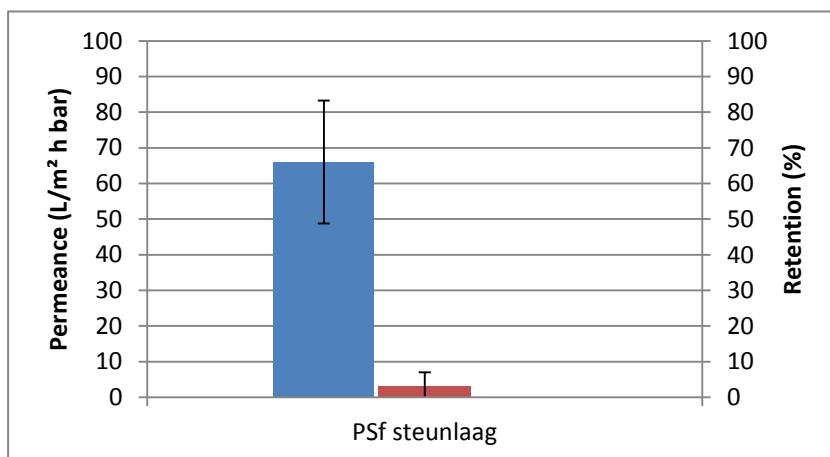


Figure 5: Results from the filtration tests using PSf supports

3.2.2. Polyimide (PI)

Preparation

Polymer solution: 14 wt% PI (Matrimid) in NMP/THF (weight ratio 3/1) or in NMP

Evaporation time: 30 s (only when THF is added to polymer solution)

Casting thickness: 200 μm

Casting speed: position 5 (0,044 m/s)

Coagulation bath: 0,5 wt% hexanediamine in milliQ-water (for simultaneous phase inversion and crosslinking)

Filtration data

Feed solution: 35 μM Rose Bengal in ethanol

Pressure: 0,5 bar

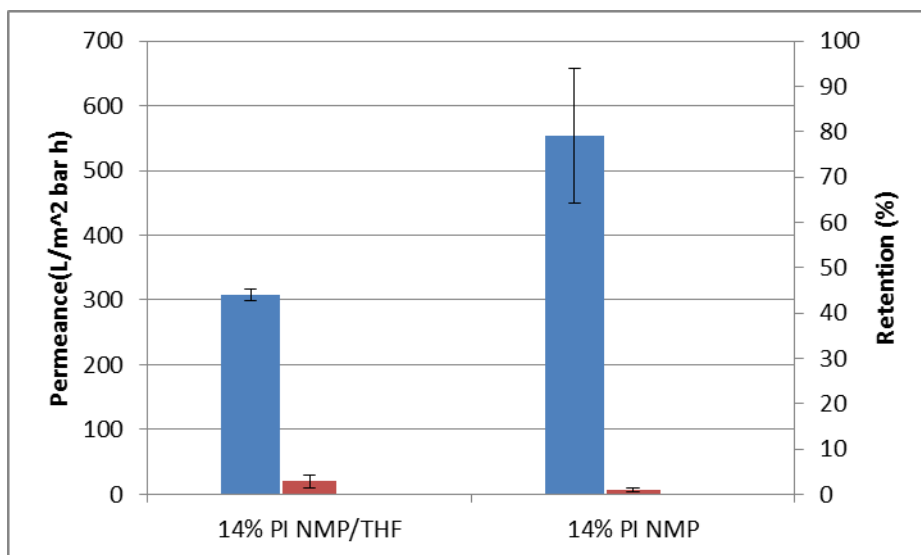


Figure 6: Results from the filtration tests using PI supports

3.2.3. Polyacrylonitrile (PAN)

Preparation:

Supports were prepared by dissolving PAN in DMSO (15 wt%) and cast on a nonwoven PE/PP support via phase inversion, followed by a hydrolysis procedure in order to convert the material to the more resistant hydrolysed PAN material. The hydrolysis was done by the immersion of the PAN support in 10 wt% sodium hydroxide at 50°C for 40 min. The remaining sodium hydroxide was removed by washing with water.

Filtration data

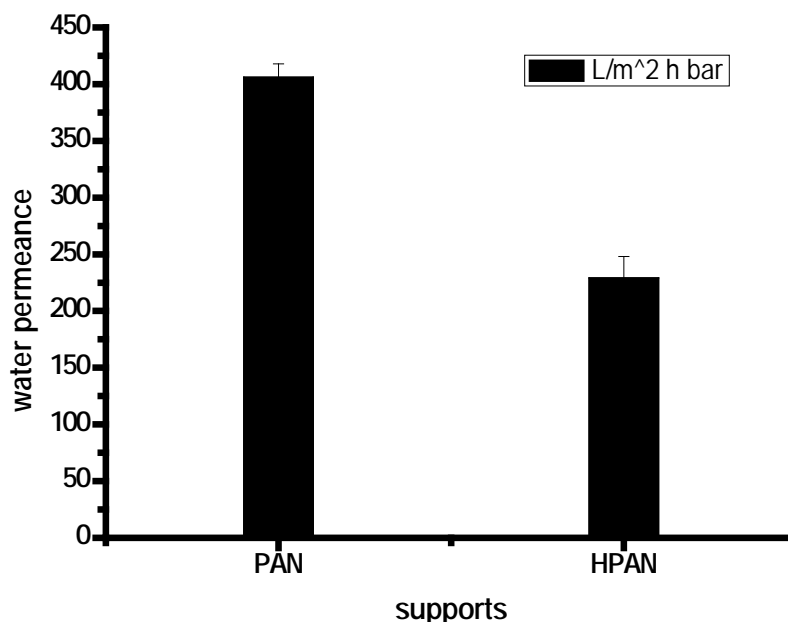


Figure 7: Results from the filtration tests using PAN supports

3.2.4. PVDF

Preparation:

Polymer : PVDF solution (MW 534 kDa) with concentrations of 6, 8, 10, 12, 14, 16 wt%
Solvent : N,N-Dimethylformamide (DMF)
Non-solvent : Demineralized water
Evap. Time : 10 sec

Pure water flux

Table 1: Filtration data for PVDF supports.

PVDF	Evaporation time	Clean water permeance	Mean pore size	Max. pore size	Surface porosity	Volume porosity	Contact angle
wt%	s	LMH/bar	μm	μm	%	%	°
6	10	1604	0.1292	0.5166	12.4	53.46	95.3±2.5
8		1474	0.0904	0.2310	13.9	47.29	84.4±5.7
10		278	0.0776	0.2629	5.4	54.74	88.2±1.7
12		407	0.0904	0.2769	9.7	45.62	90.0±4.0
14		216	0.0583	2.8383	3.9	45.09	85.1±3.6

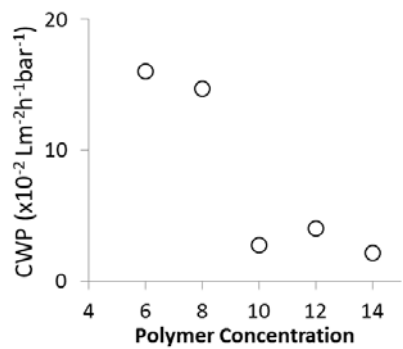


Figure 8: Clean water permeabilities of the PVDF supports prepared from different concentrations in the casting solution.

4. Benchmarking tests and standardized experimental procedures of gas membrane equipment and technology

4.1. Membrane fabrication :

For synthesis of the final PIL-membranes, the PILs will be coated on the PI cross-linked support either with a spin coater or by simply poring the PIL-solution on it. In some experiments, dense membranes will be used for comparison, prepared via solution casting with controlled evaporation.

For a dense membrane, important parameters are the following

- Concentration of the casting solution
- The choice of solvent
- Cross-linking conditions and time

For composite membranes, following additional parameters are to be considered

- Support structure
- Hydrophobicity or hydrophilicity of the support
- Selective layer thickness
- Solution coating conditions

4.2. HTGS system

On a custom-built high-throughput gas separation (**HTGS**) **system**, pure CO₂ and mixed gas selectivity and permeability values can be measured. Fig 9. shows the schematic diagram of the setup. The equipment can measure gas permeance and selectivity of 16 membranes coupons hold by a module at variable feed compositions, pressures and temperatures. Stainless steel is used as the material of construction for the HTGS membrane assembly. Feed and purge lines are 1/8 inches in diameter while the permeate lines are 1/16 inches to minimize the 'dead volume' between separation and analysis. The flow rate and composition of feed gas mixtures are adjusted by Mass Flow Controllers (MFCs), provided by Bronkhorst (Netherlands) for each gas available on the set-up. The composition of the permeate from the membranes is analyzed by a compact gas chromatograph (CGC, Interscience) and then swept by a vacuum pump (Pfeiffer Dua 2.5). The gas permeance was measured with the help of a constant volume auxiliary cylinder (maximum measurement limit of 10 mbar) which is connected to a MKS Baratron® pressure transducer. The gas flow of the MFC ranges from 0 to 1 l/min. Feed and purge lines are connected to the upper end of the membrane module via a 'Swagelock quick fit connection', while the 16 permeate lines exit from the lower end. The upstream pressure was adjusted by a back-pressure regulator mounted on the purge line.

Porous metallic plates are used as support for mounting membranes and sealed by Viton O-rings which ensure tight sealing, are compatible with different gas mixtures and possess high thermal stability. The effective permeation area of each membrane is 1.54 cm². The upstream pressure is adjusted by a back pressure regulator on the gas purge line. Purging is typically set so that 95% of the feed flow is removed as retentate, ensuring constant feed composition and sufficient feed hydrodynamics. The maximum upstream pressure for the equipment shown is 14 bar due to limitation of the applied Valco type 16-way valve. The temperature in the HT module is adjusted using an electrical resistance wire embedded in the bottom plate of the cell.⁴

Extensive efforts were put in getting the **HTGS system** operational and running accurately. This set-up had been running very well for more than 4 years, but started to show unrealistic gas selectivities about 1 year ago. This seemed to be due to a combination of hardware and software issues which took very long to all get traced and solved. For instance, calibration curves needed to be checked in detail over different concentration ranges, mass flow controllers were found to require recalibration and also needed the installation of extra back pressure regulators, the proper functioning of the MFC also required very time consuming infrastructure interventions to be performed by an external company, the GC-column needed to be reconditioned, the integration software had to be upgraded. After recalibration of all the MFC's, the gas separation results were carried out for some standard membranes, like polyimides, which gave results similar to those reported in literature.



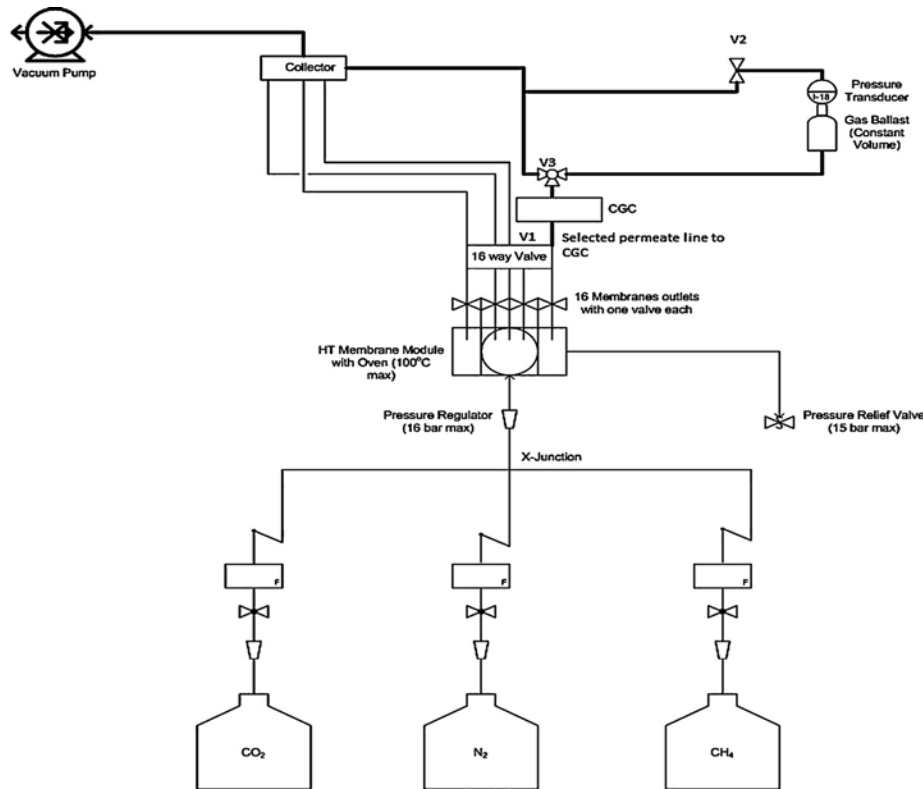


Figure 9: Schematic diagram of the HTGS system.

4.3. Membrane performance measurements

The performance of the membranes is measured on the basis of its selectivity and permeability values for a specific gas pair. The measurements steps are as follows.

- Prior the measurements, the module is evacuated by a vacuum pump some time to remove residual air and other gases. Then the gas mixture is fed into the module at the rate of 1 l/min controlled by mass flow controllers (MFC, Bronkhorst). The permeate is allowed to enter into the CGC to get peaks for both gases in CGC graphs and from those peak areas for both gases, selectivity values were calculated.
- For gas permeability measurements, valve between the auxiliary cylinder and the vacuum pump is closed down and sent to the auxiliary cylinder for expansion to measure the rate increase in pressure with respect to time (dp/dt) until it reached to steady state. The gas permeability was calculated by following equation:

$$P = \frac{273 \times 10^6}{760} \times \frac{y_i V}{AT (76/14.7) x_i P_1} \times \left(\frac{dp}{dt} \right) \quad (1)$$

where "V" is the downstream volume (cm^3) and "A" the membrane permeation area (cm^2)., P_1 is the pressure of the feed gas (psi) and T is the operating temperature (K). Mole fractions of component i in the downstream and upstream is designated by y_i and x_i are the respectively. The mixed-gas selectivity was calculated by the ratio of mole fraction of the two gases in downstream (y) and upstream (x) streams by using the following equation:

$$\alpha_{ij} = (Y_i / Y_j) / (X_i / X_j) \quad (2)$$

where x_i and x_j are the mole fractions of components i and j in the upstream respectively, while y_i and y_j are the mole fractions of components i and j in the downstream respectively. The permeability coefficient is given by

$$P = D_i S_i \quad (3)$$

where D_i and S_i are the diffusion and solubility coefficients respectively. The time lag method will be used to measure the diffusion coefficients of the gases in the polymeric film.

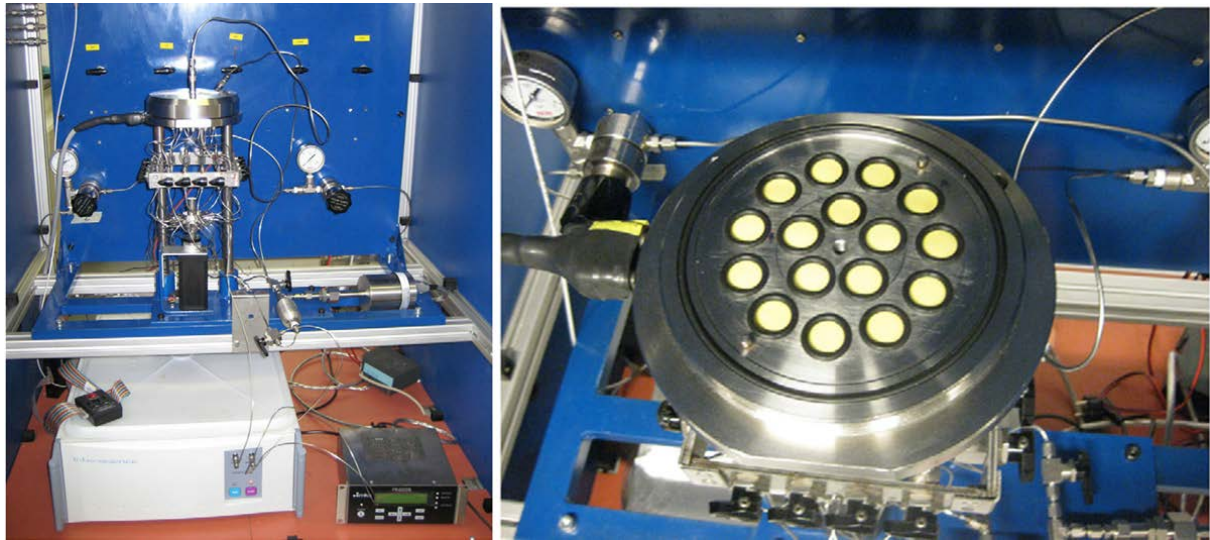


Figure 10: Overview of the full HTGS set-up with compact GC (left) and a detail of the 16 position membrane module (right).

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5. Conclusions and future directions

The HTGS set-up is now fully validated and performs very accurately and fast. The diamine crosslinked PI-support came out as best, combining excellent thermal and chemical stability with an appropriate surface tension, sufficiently low surface roughness and high surface porosity to allow uniform coating without extensive intrusion, and still showing a good permeability in order not to become rate-limiting when testing the PIL-coated membrane in the next part of this project.



6. References :

1. T. Yamaguchi, F. Miyata & S.-I. Nakao. *Journal of Membrane Science*, 214 (2003) 283 – 292.
2. S. D. Hojniak, A.L. Khan, O. Hollóczki, B. Kirchner, I.F.J. Vankelecom, W. Dehaen & K. Binnemans. *Journal of Physical Chemistry B*, 117 (2013) 15131 – 15140.
3. G. E. Romanos, L. F. Zubeir, V. Likodimos, P. Falaras, M. C. Kroon, B. Iliev, G. Adamova, and T. J. S. Schubert, *J. Phys. Chem. B*, 2013, **117**, 12234–12251.
4. S. D. Hojniak, A. L. Khan, O. Hollóczki, B. Kirchner, I. F. J. Vankelecom, W. Dehaen, and K. Binnemans, *J. Phys. Chem. B*, 2013, **117**, 15131–15140.
5. S. D. Hojniak, I. P. Silverwood, A. L. Khan, I. F. J. Vankelecom, W. Dehaen, S. G. Kazarian, and K. Binnemans, *J. Phys. Chem. B*, 2014, **118**, 7440–7449.
6. A. L. Khan, S. Basu, A. Cano-Odena, and I. F. J. Vankelecom, *J. Membr. Sci.*, 2010, **354**, 32–39.

