PROJECT FINAL REPORT

Grant Agreement number: **NMP3-SL-2009-228631**

Project acronym: ***DOUBLENANOMEM***

Project title: **Nanocomposite and Nanostructured Polymeric Membranes for Gas and Vapour Separations**

Funding Scheme: **Small or medium-scale focused research project**

Period covered: from **1 June 2009** to **31 May 2012**

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Date: **22/12/2012**

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1 Final publishable summary report

1.1 Executive summary

One of the main challenges of modern society is to contrast the effects of human activity and increasing industrialization on the earth's atmosphere, its climate, and on the health and well-being of the people and other living creatures. New technical solutions are needed to face the increasing threat of the use of fossil fuels and the release of noxious substances into the atmoshphere. At the same time novel approaches are needed to produce alternative energy fuels in a more ecologically friendly way. The DoubleNanoMem project was written out against this background, knowing that membrane technology may offer a more environmentally benign tool to solve a series of industrially relevant gas separation problems. It wishes to replace traditional processes by membrane technology, offering improved performance at equal or lower cost, with increased energy efficiency and with lower environmental impact.

The project is focused on the development and the study of novel materials with a favourable combination of high permeability and high selectivity, based on porous nanofillers embedded in high free volume (FV) polymers or polymers with intrinsic microporosity. It points at the development of novel materials with superior properties compared to current state-of-the-art polymeric membranes for a successful replacement of traditional gas, vapour or liquid separation processes by membrane processes. The use of nanocomposite and nanostructured membrane materials is seen as one of the few approaches with the real potential to achieve this goal. The project therefore covers the entire course from laboratory scale sample preparation and characterization, to membrane module construction and pilot scale application tests.

The main idea is the creation of a scientific basis for the combination of advanced polymers with suitable nanoparticles, mutually compatible and leading to membranes with unique separation properties. To achieve this aim a wide variety of polymers and nanoparticles has been tested. Several different types of nanoparticles are considered, all able to increase free volume or to create preferential channels for mass transport: both multi wall and single wall carbon nanotubes, zeolites, mesoporous silicas, cucurbituril derivatives and several metal organic or fully organic frameworks. Commercial polymers (glassy high free volume perfluoropolymers) as well as novel synthetic polymers (Polymers of Intrinsic Microporosity, PIMs, or polynorbornene derivatives) are considered.

The principle targets of the proposed project are:

- Development of membranes with tailored separation performance based on innovative materials.
- Experimental characterization and development of structure-performance relationships.
- Modelling of transport phenomena and of the material's structure to provide a better scientific understanding of gas and vapour separation processes.
- Applied research in consolidated and emerging fields of gas separation and pervaporation and demonstration of the practical applicability of the developed principles.
- Dissemination to a wide scientific as well as general public.

1.2 Project context and objectives

The concept of the DoubleNanoMem project is the use of high free volume polymers with inherent nanoscale porosity in combination with nanofillers with structured porosity to further enhance the separation performance. Radical improvement of the permeability and selectivity of the available commercial membranes are required for a successful replacement of traditional gas, vapour or liquid separation processes. Composite or nanostructured membrane materials are seen as one of the few approaches with the real potential to achieve this. An appropriate combination of high performance polymers and specific nanoparticles to form nanostructured membranes is therefore the main aim of the project.

For the realization of the project aims, an equilibrated consortium composed of universities, research centers and industrial partners was formed, coordinated by the Institute on Membrane Technology of the Italian National Research Council.

		Organization Name	Acronynm	Nation
Research organization	1	**Coordinator:** Consiglio Nazionale delle Ricerche, Institute on Membrane Technology, Rende (CS)	ITM-CNR	Italy
	2	A.V. Topchiev Institute of Petrochemical Synthesis, Moscow	TIPS	Russian Federation
Higher education	3	Delft University of Technology, Department of Bio-technology, Delft	TUD	The Netherlands
	4	Katholieke Universiteit Leuven, Department of Chemical Engineering, Leuven	KUL	Belgium
	5	Institute of Chemical Technology, Department of Physical Chemistry, Prague	ICT	Czech Republic
	6	The University of Calabria, Department of Chemical Engineering and Materials, Rende (CS)	Unical	Italy
	7	University of Manchester, School of Chemistry, Manchester	UniMan	U.K.
	9	Cardiff University, School of Chemistry, Cardiff	CU	U.K.
Industry (SME)	8	ZAO STC "Vladipor", Vladimir	Vladipor	Russian Federation
	10	Tecno Project Industriale s.r.l.	TPI	Italy

The principal idea leading to propose this project is the creation of a scientific basis for the combination of such high performance polymers with appropriate compatible nanoparticles. Since some of the base materials proposed in the project have demonstrated very promising but also unusual transport properties, further studies to extend the scientific understanding of their behaviour is fundamental. To achieve this aim, a number of carefully chosen polymers and nanoparticles will be tested. A relevant feature of this project is the idea to use nanoparticles with microcavities inside them, such as carbon nanotubes (CNT), high aspect ratio zeolites and mesoporous oxides and cucurbituril derivatives, metal organic frameworks, to create increased free volume and/or preferential channels for mass transport, through increased sorption or diffusion. In this regard they differ from nanoparticles used in previous works and in more recent studies reported at latest edition of the world's most prestigious membrane conference, ICOM2008 in July 2008 (mainly hydrophobic silica), the effect of which is "breaking the structure of polymer matrices". Porous nanoparticles should increase permeability, but not at the expense of permselectivity, as some studies demonstrate.[1] In some cases, in particular for pervaporation (PV), also non-glassy polymers but with proven superior intrinsic performance will be tested as materials of the matrices.

The main S&T objectives of the project can be summarized as:

- Synthesis of novel high-free volume polymers and compatible inorganic and carbon nanofillers
- Development of membranes and modules with tailored separation performance based on innovative materials
- Experimental characterization and development of structure-performance relationships
- Modelling of transport phenomena and of the material's structure to provide a better scientific understanding of gas and vapour separation processes and to accelerate the development work.
- Applied research to favour exploitation in emerging fields for environmental technology.

A justified selection of the nearly infinite number of possible combinations of polymers and nanofillers will be made at the beginning of the project and will be further refined in the course of the project. The overall aim of the project is to make membrane technology a more competitive technology, able to replace traditional processes by offering improved performance at lower cost, with increased energy efficiency and lower environmental impact.

The focus of the present project will be on new material development, control of nanostructure and tailoring of permeation properties, in view of some specific applications. The envisaged application fields are numerous and a selection is given in the list below.

- Isolation of biofuels from fermentation broth, for sustainable energy production
- CO_2 separation from flue gas, for instance from power generation plants, to reduce the carbon dioxide footprint of such installations.
- Sweetening of natural gas and/or biogas for cleaner and more efficient use of this energy source.
- Natural gas treatment by membranes with improved selectivity towards higher hydrocarbons and nitrogen
- Air separation to produce oxygen enriched air for medical and industrial applications.
- H_2 recovery from syngas or from off-gas from butanol fermentations for sustainable energy production

All these applications have important environmental implications, treating problems related to sustainable energy consumption (e.g. CH_4 production and separation, CO_2 sequestration and disposal, global warming, Kyoto protocol) and sustainable energy production (e.g. H_2 production and separation, biofuel production by fermentation), and are therefore of great significance for the EC's strategic position.

Newly prepared membranes will always be subjected to a rapid wide screening of the transport properties to foresee their potential in different fields. The purpose is to focus on a maximum of 3 to 4 main topics, involving at least bioethanol separation and CO_2 separation, and probably another area of major industrial interest, like natural gas processing. This decision should ideally be taken in the course of the first year of the project, so that the project is more focused in the second phase.

Besides the topic Nanostructured Membrane Material addressed, the project shows a strong affinity with the topic Processing and upscaling of nanostructured materials. However, upscaling itself is not an explicit scope of the present project. Nevertheless, in the course of the project some membranes will be prepared at larger scale to enable module production with sufficient surface area to be used in the planned feasibility and application tests.

Facing the problems of greenhouse gas emissions (CO_2 separation) and biogas and bioethanol production the most relevant other topics addressed by the project are Energy and Environment.

1.3 Main Science & Technology results/foregrounds

The need to decrease the huge energetic cost of commodities, the effective production of fuels from fossil sources or biomasses, the search for sustainable and non polluting processes, they all demand more resistant, more selective and more permeable membranes which, at the same time, are as cheap as today's commercial polymeric membranes. Mixed matrix membranes, in which selective porous particles are dispersed in a polymeric matrix, are a viable option to overcome the poor permeability and selectivity of polymeric membranes.
Unfortunately the homogeneous dispersion and the adhesion of very small porous particles (less than 1 micron) in a thin polymer films is a difficult task, much more difficult than dissolving a teaspoon of lyophilized coffee in a cup of milk. Especially when your polymer is similar to Teflon - probably one of the most repellant materials known today - and when you wish to keep the pores of your particles wide open.
How do you disperse and adhere little tiny hydrophilic porous particles in a strongly hydrophobic polymer, and at the same time not plugging the pores of your particles? The answer is chemistry. The team of Unical has solved this problem for instance by developing its own technology for virtually each polymer that can be used for making membranes with inorganic fillers[2], while the team of UniMan has chosen the approach to use organic[3] or metalorganic fillers.[4] This forms the basis of the bulk of the work on MMMs, while the teams of TIPS, CU and Uniman are responsible for the preparation of special tailor-made high free volume polymers. The remaining teams are mainly involved in the membrane preparation, characterization and their final application.

1.3.1 Novel high-free volume polymers

Polymers of intrinsic microporosity (PIMs) are polymers with rigid, contorted macromolecular backbones that cannot pack efficiently in the solid state and so trap a large amount of interconnected free volume. These polymers behave as molecular sieves ("microporous materials", pore dimensions <2 nm, as defined by IUPAC in the context of adsorption studies). Membrane-forming PIMs exhibit high permeability in combination with good selectivity. This very interesting family of polymers was developed about 1 years ago by pioneering work of Peter Budd and Neil McKeown, now teamleaders of UniMan and CU. On the other hand, the team of TIPS developed great expertise in norbornene-based high free volume polymers. The main players in the polymer synthesis activities are therefore the teams of TIPS, UniMan and CU.

1.3.1.1 Monomer synthesis, purification and analysis for new PIMs and PIM-PIs

The DoubleNanoMem project developed new monomers for PIMs, with the aim of tailoring both the intrinsic properties of the PIM and the interactions with nanofillers.
At UniMan and CU, dianhydrides incorporating spiro-centres were synthesised for use in the preparation of new PIM-polyimides (PIM-PIs).
To be suitable for membrane applications, a polymer must meet a number of requirements, including solubility in solvents that are suitable for processing, and an optimum molar mass, to give a membrane with adequate mechanical properties. At UniMan, new monomers were developed to create novel PIM-polybenzimidazoles (PIM-PBIs), but membranes suitable for permeation studies were not achieved within the timescale of the project.

1.3.1.2 Synthesis of Novel functionalized PIM-1s

PIM-1, the archetypal membrane-forming PIM, remains the most promising member of this class of polymer for scale-up and commercial use.

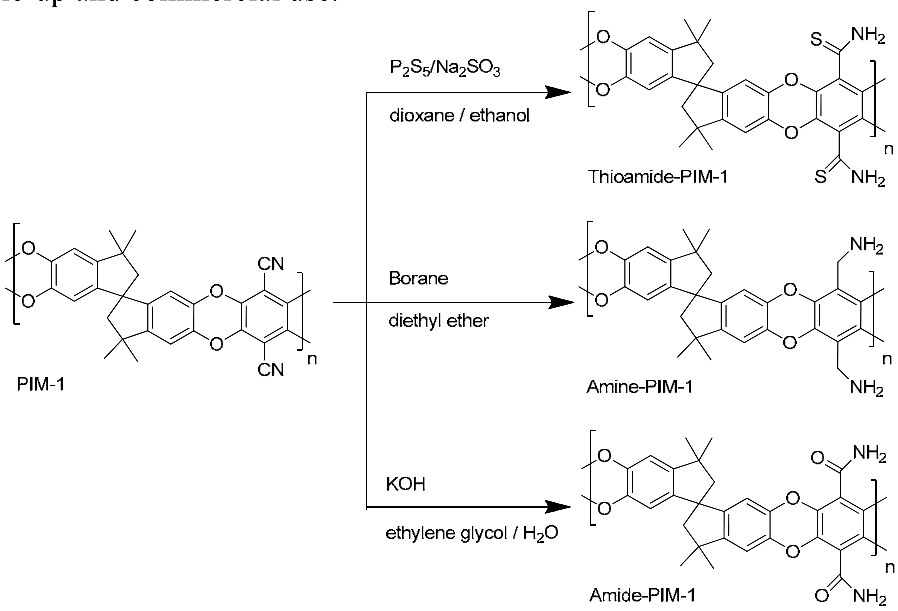


Figure 1.1. Chemical modification of PIM-1.

Quantities of PIM-1 were prepared at UniMan and distributed to partners. A number of chemical modifications of PIM-1 were investigated, including conversion to thioamide, amine and amide forms (Figure 1.1.). A paper on the thioamide modification has been published[5] and papers on other modifications are in preparation.

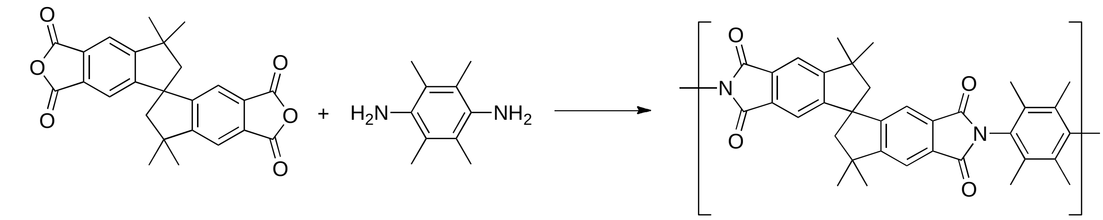
1.3.1.3 Preparation of block copolymers suitable for use as compatibilizers

A block copolymer comprising a block in common with the polymer matrix and a block with affinity for a nanofiller is in general expected to improve adhesion at the interface between polymer and filler. However, in initial experiments with PIM-1, it was found that for a high free volume polymer this is counteracted by the strong adsorption capacity of the internal surface area of the polymer. Consequently, no further work was carried out on this task.

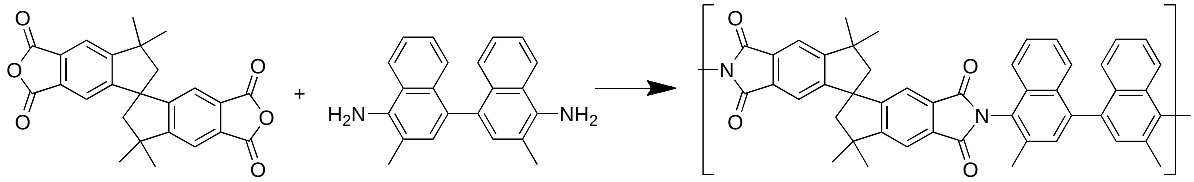
1.3.1.4 Synthesis of novel PIM-Polyimides

The synthesis work at UniMan and at CU progressed as planned with the synthesis of many film-forming, novel polymers demonstrating intrinsic microporosity (PIMs). A number of novel PIM-polyimides (PIM-PIs) were prepared. At UniMan, a major focus was the development of PIM-PIs with ortho-positioned hydroxyl groups to allow the thermal rearrangement to polybenzoxazoles. Both chemical and thermal routes to PIM-PIs were explored. Thermal rearrangement was shown to enhance both adsorption and permeation properties.

At CU the synthesis of a number of new PIM-Polyimides (PIM-PIs) from two novel bisanhydrides (**1** and **2**) was completed. Polyimides derived from spirobisindane bisanhydride **1** and two appropriate aromatic diamines, which had previously been shown to give permeable polymides, gave PIM-PI-9 (RY-45) and PIM-PI-10 (RY-177), shown below. Both of these PIM-PIs showed excellent film-forming properties and proved highly permeable but demonstrated less ideal selectivity than PIM-1.

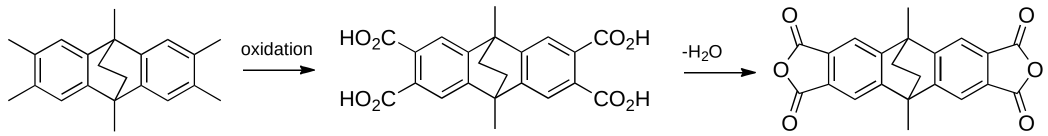


PIM-PI-9



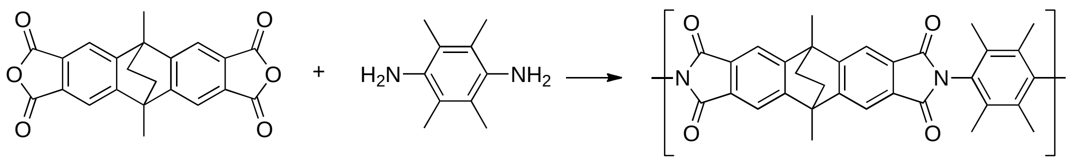
Bisanhydride **1** PIM-PI-10

Bisanhydride **2** contains the very rigid bridged bicyclic components ethanoanthracene (EA) and was prepared from the appropriate hydrocarbon as shown below.



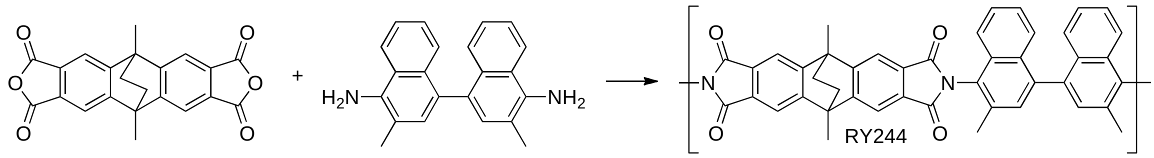
Bisanhydride **2**

The polyimides prepared from bisanhydride **2** using the same aromatic diamines, as shown below, were denoted PIM-PI-11 (RY-222) and PIM-PI-12 (RY-244).



PIM-PI-11

Unfortunately, PIM-PI-11 polymer proved insoluble in all solvents and therefore a film suitable for gas permeability studies could not be made.

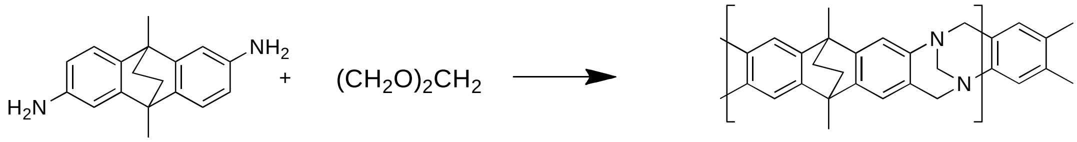


PIM-PI-12

However, PIM-PI-12 is a soluble polymer of very high molecular mass (M_n = 100,000; M_w = 300,000 by GPC), which was used to make a robust thin film for gas permeability measurements at ITM. This polymer proved to have high gas permeability and higher ideal selectivity than PIM-1 and is, we believe, the first polyimide to demonstrate data that lies above the updated 2008 Robeson upper bound for most important gas pairs (O_2/N_2; H_2/N_2, H_2/CH_4; CO_2/N_2 and CO_2/CH_4) see below.

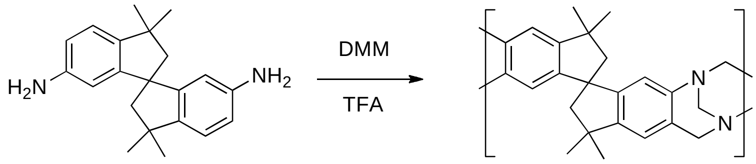
1.3.1.5 Synthesis of novel Troger's base derived PIMs

Some novel polymers using Troger's base formation from an ethanoanthracene-based diamine and dimethoxymethane (DMM) in trifluoroacetic acid (TFA) were produced to give a polymer (PIM-EA-TB) of high apparent surface area (1000 m^2 g^{-1}). This new polymerisation reaction, based on a reaction known for over 100 years, has been optimised to provide polymers of high molecular mass (M_w > 100 000) suitable for the formation of robust solvent-cast films for gas permeation studies.



PIM-EA-TB

This polymer has a unique structure in that is composed only of benzene rings linked by rigid bridged bicyclic units and is, therefore, highly shape persistent even compared to other PIMs. For comparison with existing PIMs, the equivalent spirobisindane-based polymer (PIM-SBI-TB) was prepared as shown below.

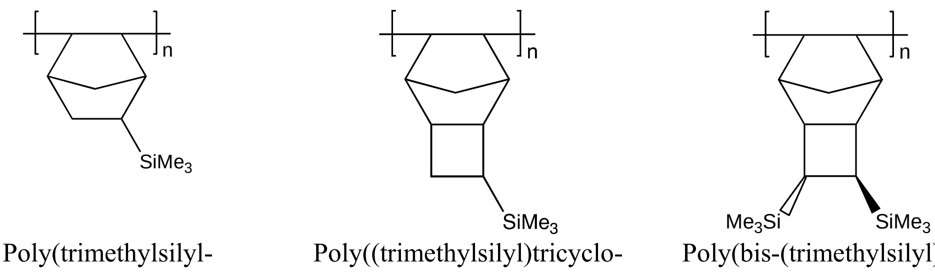


PIM-SBI-TB

High quality films of PIM-EA-TB and PIM-SBI-TB were provided to ITM and those of the former showed very high permeabilities and extraordinary selectivities particularly for gas molecules with small kinetic diameters (e.g. H_2, He, and O_2). The means that its data lie well above the updated 2008 Robeson upper bound, a universal performance indicator to assess the potential of new polymers for gas separations, for a number of important gas pairs (O_2/N_2, H_2/N_2, H_2/CH_4 and H_2/CO_2). Comparisons with the data for PIM-SBI-TB, which is typical for a PIM and contains the relatively flexible spirobisindane units, indicate that the remarkable performance of PIM-EA-TB as a molecular sieve can be attributed to the extreme shape-persistence of the combined use of the bridged bicyclic components (EA and TB). This conclusion is consistent with the exceptional performance of PIM-PI-12 (above), which also contains the ethanoanthracene bridged bicyclic unit.

1.3.1.6 Novel norbornene-based high-free volume polymers

The work of the team of TIPS was focused on the preparation of novel addition type norbornene derivative polymers Three polymers containing $Si(CH_3)_3$ groups were successfully prepared. Their chemical structures are shown below.



Poly(trimethylsilyl-norbornene) (I) | Poly((trimethylsilyl)tricyclo-nonene) (II) | Poly(bis-(trimethylsilyl)tri-cyclo-nonene) (III)

The novel high free volume polymers belonging to the class of poly(tricyclononenes) were synthesized via addition type polymerization of Si-substituted cycloolefins in the presence of nickel(II))naphtenate/MAO catalyst (polymer I) and $Pd(OAc)_2/B(C_6F_5)_3$ catalyst (polymers II and III).

Molecular characterization of polymers synthesized by all teams was carried out by multi-detector Gel Permeation Chromatography (GPC) and other techniques as appropriate. All polymers were thoroughly characterized to confirm their structure and to evaluate molar mass parameters.

The gas permeabilties of most of the novel polymers were measured by ITM and TIPS, and the gas and vapour sorption by ICT (below).

1.3.2 Novel selective nanofiller particles

The work on nanofiller synthesis and modifications involved mostly the teams of ITM-Pd (Padua section), TIPS, ICT, Unical and UniMan.

1.3.2.1 CNT preparation and functionalization

Multiwall carbon nanotubes (MWCNTs) were synthesized and modified with $-NH_2$ groups by ball milling in a NH_3 atmosphere in the group of Prof. J.B. Nagy of Unical. The same purified CNTs were oxidized, cut and modified by -nC18, -PEG5000, triethylene glycol and perfluorinated chains by the Padua section of ITM, while fluorination was carried out by TIPS. A carpet of aligned CNT was prepared on alumina impregnated with a Co-Fe catalyst with a N_2/C_2H_4 flow at 700°C.
The activity of ITM-Pd was focused on the study of the purification procedures for raw carbon nanotubes (CNTs). These procedures involve the use of aqueous acidic treatments, with the aim of obtaining a material purified from amorphous carbon and metal particles, and mainly formed by shortened nanotubes bearing carboxylic moieties suitable for subsequent functionalizations to allow dispersion in the polymer matrix. In the first series of experiments on commercial single walled nanotubes it was found the best purification route, and the importance of a treatment called *etching* was underlined. Based on this experience, a study on the purification of MWNTs produced by Unical has been pursued: the use of sulphonitric treatment was found to be the best purification procedure for these CNTs. The purified CNTs were functionalized with octadecylamine and amino-PEG5000, obtaining derivatives with good solubility in toluene and dichloromethane. To improve the selectivity of the filler for CO_2 with respect to N_2 or CH_4, a functional group bearing a free amine at the edges of the pore was then introduced. Compatibility between CNTs and the polymer matrix was promoted by 1,3-dipolar cycloaddition of azomethine ylides to the carbon nanotube walls. A model reaction run in three different solvents (DMF, NMP and NCP) was useful to determine the importance of 1-cyclohexylpyrrolidin-2-one as a dispersant for crude nanotubes. The 1,3-dipolar cycloaddition of different classes of compounds (aziridines, imines and oxazolidinones) was investigated. The functionalization of CNTs with an imine precursor yielded the better dispersed material (in DMF). With the aim of increasing the compatibility of the filler with fluorinated polymers, a (heptadecafluoro)octyl phenyl derivative was obtained upon a diazotation reaction at the sidewalls of the tube. The synthesis of CNTs derivatives was carried out in a commercial flow reactor (ACR Coflore®): this tool is a promising way to control the degree of functionalization of an heterogeneous material such as CNTs. Furthermore, continuous flow processes are intrinsically easy to scale up, leading to rapid functionalization of relatively big amounts of nanotubes.

1.3.2.2 Macrocyclic nanofiller preparation, modification and characterization

The ICT group obtained several macrocyclic ring-shape nano-additives: *cucurbit[6]uril, decamethylcucurbit[5]uril, bambus[6]uril* and new functionalized derivates *octabenzylbambus[4]uril* and *dodecabenzylbambus[6]uril*. These new macrocyclic derivates were synthesized with 4 (n=2) and 6 (n=3) ring member macrocyclic molecules (Figure 1.2.), derived from the *bambus[n]uril* structure. In comparison with original CH_3 groups on nitrogen atoms in *bambus[n]uril* molecule and with limited solubility of *cucurbit[n]uril* based nanoparticles, new derivates with bulky side-groups exhibited improved solubility in common organic solvents. Such property is important for suppressing undesirable (polymer/additive) phase separation and particle clustering during preparation of mixed matrix membranes.

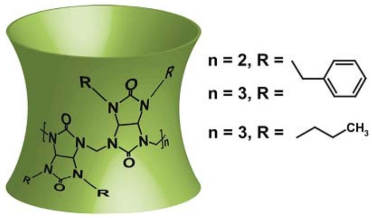


Figure 1.2. Schematic draw of bambus[n]uril derivates.

1.3.2.3 Inorganic nanofillers

Molecular sieves and mesoporous oxides were prepared by the team of Unical in different size, shape and aspect ratio (AR, largest-to-shortest dimension ratio), and were modified a) to make them compatible with the polymer phase; b) to improve the sorption selectivity of the filler. The functionalization leaves the specific surface of the fillers almost unchanged and does not occlude the pores. A sharp decrease of the specific surface and even pore plugging are instead very common with other methods[6]. SAPO-34 (CHA) was chosen due to its excellent selectivity to CO_2, and crystals with aspect ratio up to 16 were prepared by means of crystal growth inhibitors; silicalite-1 (MFI) because of its high ethanol/water selectivity; mesoporous silicas with 1-D and 3-D pore systems and wide range of pore sizes because of the openness of the porous network and for the opportunity to chemically modify the pore surface: basic groups were introduced in order to improve the affinity to CO_2, alkyl moieties to impart hydrophobicity to the pores. The CO_2/CH_4 sorption selectivity of SAPO-34 was optimized by a low Si/Al ratio and a high N/Si ratio. An overview of the above fillers is given in Table 1.1. About fifty different samples of inorganic fillers and membranes were delivered to the other consortium members for the preparation of dense and supported MMMs, for the study of the transport properties and of free volume.

Table 1.1. Properties of the inorganic fillers prepared by Unical.

	Molecular sieves		**Mesoporous silicas**			
	SAPO-34	Silicalite-1	SBA-15	SBA-16	SBA-14/SBA-11	SBA-12
Pore size (Å)	3.8	5.5 - 5.7	67	32	22	24
Particle size (μm) **and morphology**	2, 1.5, 0.5, 0.2 AR 1.2-16	15, 1.5, 1.0, 0.35, 0.18	0.8, AR 3	5	5-50 (aggregates)	5
BET Specific surface area (m^2/g)	479	390	845	987	697	902
Structure	CHA	MFI	1-D Hexagonal (*P6mm*)	3-D Cubic (*Im3m*)	3-D,Cubic (*Pm3m*)	3-D hexagonal ($P6_3/mmc$)
Functional groups	$-R_f$ $-C_2H_4Ph$ $-NH_2$	$-R_f$ $-C_2H_4Ph$ -C1 -nC18	-nC18 $-NH_2$ (excess)	-C1 -nC10 -nC18 -nC18/-nC10		

1.3.2.4 Organic and metal-organic nanofillers

As an addition to the original work plan, the group of UniMan prepared and characterized an extensive range of metal-organic frameworks (MOFs) in both large (micron scale) particle and nanoparticle form, for incorporation into mixed matrix membranes. MOFs prepared at UniMan included ZIF-8, HKUST-1 and MIL-101. Furthermore, it supplied various other fillers, via external collaborations and most of these fillers were incorporated into PIM-1 membranes (further discussion in section 1.3.3).

1.3.3 Development of membranes and membrane modules with tailored separation performance

Membrane preparation was one of the major tasks in the project, involving the largest number of teams. The teams most involved were the polymer and filler producers, TIPS, Unical, UniMan and CU, as well as the teams heavily involved in characterization (ITM and ICT). In addition to these six teams, the industrial partner Vladipor was responsible for large scale membrane production.

1.3.3.1 Neat high free volume polymer membranes

Flat sheet dense membranes of the neat polymers were prepared according to a controlled solvent evaporation of casting solutions of different polymer types in appropriate media. Polymers with intrinsic microporosity (PIM-1, PIM-PIs, chemically functionalized PIM-1 and various other PIM analogs) synthesised by Uniman and CU, and polynorbornene analogs by TIPS and commercial perfluoropolymers (Teflon AF and Hyflon AD) were used, all having high free volume. As reference for the development of composite and mixed matrix membranes, highly CO_2 selective commercial Pebax® 1657 was used too, while SBS was investigated as an alternative rubber material for PDMS in pervaporation applications. These membranes were prepared to support the activity of membrane module preparation.
The polymers studied as individual materials and components of MMMs included: PIM-1, numerous PIM analogs, copolymer SBS, poly(tricyclononene)s with one or two $SiMe_3$ groups, poly(hexafluoropropylene), perfluoropolymers such as Hyflon AD. As nano-particles different molecular sieves (SAPO-34, silicalite-1), mesoporous SBA-15, metal-organic frameworks or MOF (ZIF-8, MIL-101, HKUST, etc.), carbon nanotubes (CNT) were studied. Membrane samples prepared from additive poly(3,4-bis(trimethylsilyl)tricyclononene-7) and poly[3,4-bis(trimethyl-silyl)tricyclononene-2] were based on the catalytic system $Pd(OAc)_2/B(C_6F_5)_3$.

1.3.3.2 Mixed matrix membranes

For the CNT-based MMMs prepared at TIPS, carbon nanotubes were functionalized, jointly with Moscow State University, by carboxylation with subsequent addition of C_{18} amines with formation of tethered amide. The functionalized (C_{16}) CNTs were added to $[CH_2\text{-}CH(SiMe_3)]_n$ (PVTMS), testing the role of ultra sound (US) in obtaining stable dispersions and application of joint or separate casting solutions. Brittle films, not suitable for permeability measurements, were obtained without ultrasound treatment.
Very good combinations of permeabilities and permselectivities were obtained for the system PIM-1/HKUST (Figure 1.3.). The results are nearly as good as the obtained data for the MMMs based on PIM-1/ZIF-8.[4] Also good results were obtained for MMMs based on PIM-1 with additives of MOFs such as MIL-101, Mg-MOF-74 and others. Indeed, on several Robeson diagrams the data points are located above the Upper bounds of 2008. The reason for this behaviour is the excellent performance

of PIM-1 as the matrix polymer in combination of the beneficial effect of the MOFs. A comparison with the literature indicates that not all nano-particles give such good results in PIM-1 based MMMs.

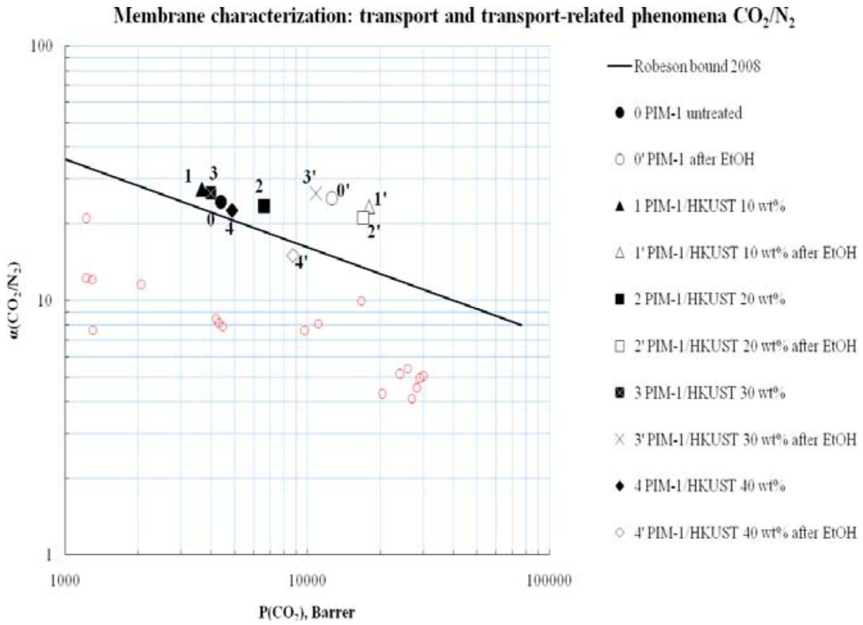


Figure 1.3. Example of a Robeson diagram for the CO_2/N_2 separation. Results for PIM-1/HKUST mixed matrix membranes.

The ICT group prepared over 50 MMMs based on macrocyclic nanofillers PIM-1 (from UniMan) and in commercial styrene/butadiene/styrene copolymer (SBS) with potential for gas/gas and gas/vapor (and eventually vapor/vapor) separations. Flat membranes were prepared by solvent evaporation (THF, chloroform and mixtures of chloroform with methanol) under optimized conditions to reach stable, self-standing, non-fragile and non-adhesive samples. The MMMs based on PIM-1 and SBS with nanofiller loading from 5 to 60 wt% were prepared by the same method where solid additives were dosed into the polymer solution.

At UniMan, besides the neat polymer membranes prepared by solvent-casting from novel PIMs and PIM-PIs, MMMs were prepared from PIM-1 with a wide range of fillers, as indicated in Table 1.2.

Table 1.2. Mixed matrix membranes prepared at **UniMan** with PIM-1 as the polymeric phase.

Filler	**Supplier**	**BET Surface Area** (m^2/g)	**Particle Size**	**Filler content** wt relative to polymer (100)
Carbon nanotubes	UniCal			15, 20, 40
Silicalite-1		390	350 nm	10, 40
Phenethyl silicalite-1		330	350 nm	10, 40
Phenethyl silicalite-1		360	180 nm	10, 25, 40
SAPO-34 aspect ratio=10		625	1 μm	10, 25, 40
SAPO-34 aspect ratio=2.2		510	1 μm	40
Zeolite 13X	Edinburgh	390		10, 20, 40
ZIF-8	UniMan	1700	2-10 μm	10
NanoZIF-8		1200	20-80 nm	16, 32, 48, 64
HKUST-1		1400	2-10 μm	10, 20, 30, 40
NanoHKUST-1		1400	40-80 nm	10, 20, 30, 40
MIL-101		2640	75- 200 nm	10, 20, 30, 40
NanoMIL-101	Bath	2845	50 nm	10, 20, 30, 40
Mg-MOF-74	UniMan	700		10, 20, 30
Mg-CPO-27 modified	St. Andrews	295		10, 25, 40
Organic cage CC3	Liverpool	625	4-14 μm	5, 10, 20, 30
Organic cage CC3 reduced				10, 20, 30
Nanocage		774	90 nm	20, 30

Since large scale preparation of PIM-based MMMs is a challenging task, as an alternative approach to enhance the membrane transport properties the incorporation of ionic liquids (IL) in commercial polymers was also investigated.[7] Stable IL gels are formed both in Viton fluoropolymer and in Pebax® poly(ether-amide).

1.3.3.3 Thin film composite membranes and their modules

In view of the preparation of membrane modules with sufficient surface area for application tests, different types of composite membranes with thin selective layers were prepared both as flat sheet and hollow fibers. They were tested mainly for the mixtures containing CO_2 or for the individual gases. On the basis of the results achieved in the preparation of self supported MMMs, supported composite membranes were manufactured from the most interesting filler-polymer combinations and then assembled in small modules. Pre-treatment of the support to avoid the infiltration of the polymer was successfully adopted for certain dilute dope solutions. The casting of selective layers, carried out according to different protocols (*e.g.*, dip-coating, roll coating for flat film supports, cross-flow filtration for hollow fiber supports), produced selective samples. In some cases, relatively large permeances of CO_2 up to 6-7 ($m^3/(m^2$ h bar)) were obtained in the case of CNT loaded in PIM-1.

The on-line spinning with a triple orifice spinneret, carried out to obtain Pebax-based thin film composite hollow fibers in a single step, was not successful yet. This procedure yielded porous membranes and needs further optimization.

JSC STC "Vladipor" was responsible for the preparation of suitable flat sheet membranes to be used as supports for composite gas separating and pervaporation membranes at ITM. Composite flat sheet membranes were produced using PIM-1 produced by UniMan and the fillers obtained from UniCal. The work of Vladipor at pilot scale was supported by the development of lab scale samples and development of preparation protocols at ITM. Finally, the composite membranes produced on a pilot plant were assembled as spiral-wound separating modules.

Flat sheet supports

The most successful flat sheet supports were based on the fluoropolymer Fluoroplast-42 (F-42, a copolymer of vinylidene fluoride and tetrafluoroethylene). They were produced at a 50 m^2 scale on a pilot plant, using the so-called dry phase inversion method, in which the low-volatile nonsolvent is present in the casting solution and no coagulation bath is used. The smallest pore size reached, approx. 50 nm, was most suitable for the TFC membrane preparation.

Some supports were used to produce composite membranes with selective layer based on the commercial polymers (*e.g.*, SBS, Pebax® 2533 and Pebax® 1657) on the JSC STC "Vladipor"'s pilot plant (Figure 1.4.).

Samples of microfiltration membrane based on polyethersulfone with pore size of 0.22 microns were prepared as well and sent to UniMan and ITM.

Regenerated cellulose supports were less suitable for use as supports, because these films, normally used for liquid filtrations, form large cracks upon complete drying. Therefore TFC preparation was unsuccessful.

Composite flat sheet membranes

The use of intermediate layers based on silicon organic block co-polymer and poly(etherurethane-urea) on a support of F-42 with pore size of ~ 50 nm greatly improved the production of membranes with an SBS selective layer. The intermediate layers were cast from micellar solutions of the two selected polymers. Samples of both were produced on a pilot plant in the quantity of 2.5 m^2. This work allowed the development methods of preparing composite membranes with selective layers on the basis of Teflon AF 2400 filled with zeolites (UniCal) and PIM-1 (UniMan).

Preparation on a pilot plant of ca. 1.5 m^2 of composite mixed matrix membranes based on (Teflon AF2400 + 25 % MFI) allowed the preparation of a lab sample of a spiral-wound module with an active area of 0.25 m^2. However, permeation tests at ITM of the A4 sheet membranes showed that in these samples the silicone layer determines the transport resistance and that the Teflon/MFI layer does not contribute significantly to the overall transport. Lab samples of membranes of Teflon AF2400+25% MFI, without the intermediate silicon organic layer showed no significant effect of the MFI on the transport, but the MFI appeared to promote the formation of a defectless Teflon AF2400 layer.

Figure 1.4. Pilot-industrial plant of JSC STC “Vladipor” for production of composite membranes.

Composite neat PIM-1 membranes were cast from a stable micellar PIM-1 solution and sequential one side coating of the solution onto the 50 nm F-42 support yielded ~ 1.5 m^2 of the membrane, which was further scaled-up at the pilot plant. Considerable reduction of the permeance in time was observed for these membranes.

The combination of PIM-1/functionalized MFI yielded supported mixed matrix membranes successfully. Recipes and conditions of preparing lab samples of composite membranes based on PIM-1+20 % MFI were developed by ITM and were found to be highly selective. However, large size samples of the same composition produced on the pilot plant in the amount of 4 m^2 appeared to be less selective.

The main results achieved by JSC STC “Vladipor” can be summarized as:

- Development of recipes, preparation conditions and preparation on a pilot plant of membranes based on Fluoroplast F-42 with various pore sizes. A lot of membranes with pore size of 50 nm, flat sheet width of 300 mm was produced on a pilot plant in the amount of 50 m^2.
- Development of recipes, preparation conditions and preparation on a pilot plant of composite membranes based on SBS polymer with intermediate layers from silicon organic polymer and polyetheruretaneurea.
- Development of recipes, preparation conditions, preparation and scale-up to pilot scale of composite membranes based on (Teflon AF 2400+25% MFI), on PIM-1 and on (PIM-1+MFI).
- Development of recipes and preparation conditions, production of lab samples and scale-up to pilot scale up to 70 m^2 of composite membranes based on Pebax® 2533 and Pebax® 1657.

Spiral-wound modules

Spiral-wound SBS membrane modules with an area of ~ 0.25 m^2. (Figure 1.5.) were prepared, using two different intermediate layers (silicon organic block co-polymer and poly(etherurethaneurea)) to support the SBS selective layer on the F-42 support membranes (pore size ~ 50 nm). The modules were supplied to ITM for gas separation and pervaporation tests, together with vessels and accessories.

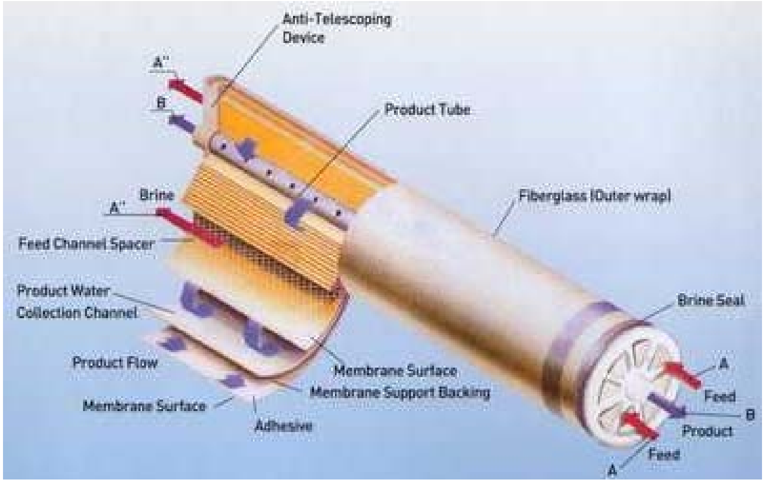


Figure 1.5. Exploded image of a spiral-wound module.

The PIM-1 composite membrane was used to make a spiral-wound element with an active area of 0.25 m^2 (Figure 1.6.). A lab sample of spiral wound element from membrane based on PIM-1+20 % MFI was produced.
Other modules were prepared with the highly CO_2 selective Pebax 1657. Careful optimization was needed to avoid membrane damage by sticking of Pebax® to itself. For this purpose different materials were tested for the spacer net used in the modules. The largest Pebax module had a surface area of ca. 5 m^2 and was used for application tests in the pilot setup of TPI. A module was cut in two perpendicularly, for the exhibition, to show the cross-section of the spiral and the flow profile of the feed and permeate gas streams. In the last month of the project, new samples PIM-1 and MFI were supplied to Vladipor by UniMan and by Unical, respectively, and the last modules will be prepared beyond the end of the contract.

Figure 1.6. Images of a pressure vessel, containing a PIM-1 based spiral-wound module.

The main results achieved by JSC STC “Vladipor” on membrane module preparation can be summarized as:

- Development of a design and preparation of lab samples of spiral-wound type elements from SBS based membranes, from (Teflon AF 2400+25% MFI) based membrane, from PIM-1 and from (PIM-1+MFI) based membrane.
- Optimization of the design of the spiral-wound modules, which allowed to minimize negative effect of mechanical loads, generated in production and testing of elements, on the integrity of selective layers.
- Development of a large scale of spiral-wound based on Pebax® 1657.
- Demo materials were prepared for the exhibition during the DoubleNanoMem Workshop.

Poly(acrylonitrile) and poly(vinylidene fluoride) hollow fibers were developed at ITM as porous supports with a proper morphology and pore size distribution to guarantee stable and defect-free polymer thin layers upon coating. The preparation was based on the non-solvent induced phase separation process according to the dry-wet spinning technique.

These supports were coated with SBS, glassy amorphous perfluoropolymers and PIM-1.
Bench-scale modules (ca. 25 cm2) based on composite hollow fibre membranes were also prepared at ITM. The composite membranes were prepared by dip coating of PAN porous hollow fibre supports ad hoc prepared in a PIM-1 solution.
Alternatively, nanofiltration membranes were developed, which could in principle be applied in the pre-treatment of the pervaporation broth and which, in the present case, were also suitable for use with organic solvents.8

1.3.4 Experimental investigation and modelling of the membrane structure and their transport properties

1.3.4.1 Structural and transport related properties

All membranes were subjected to thorough general and structural characterization. The effects of ethanol treatment of the membranes, known to swell them and to remove traces of solvent, and the subsequent aging behavior were explored. Virtually for all the systems soaking of membranes in EtOH resulted in a significant growth of permeability, though reduction of permeability in time was observed.

The use of gas sorption analysis of glassy polymers, as a novel approach for testing free volume and characterization of their nanostructure. This technique was pioneered at UniMan. N_2 and CO_2 were used as molecular probes to characterize high free volume polymers and nanocomposite membranes prepared by other teams, and PIMs prepared by UniMan itself. This analysis was also applied separately to the nanofillers and to the membranes with nanofillers.

The Positron Annihilation Lifetime Spectroscopy (PALS) method was applied to study the physical aging of PIM-1 and PIM-1/ZIF-8 membranes by TIPS, in collaboration with the Institute of Chemical Physics (Moscow). The change of free volume caused by the addition of ZIF-8 in PIM-1 was studied and data were also compared with a novel PIM from CU (PIM-EA TB).
The study of PIM-1 showed that the PALS parameters were not much affected by physical ageing in the first 140 h after film casting and alcohol treatment. Search in the literature showed that aging of different glassy polymers is normally accompanied by either decreases in lifetimes (hole radii) or absence of the changes of these values. In MMM films based on PIM-1/ZIF-8, prepared by UniMan with a ZIF-8 concentration up to 43%, four component lifetime spectra were observed, which is a common characteristic for materials with large free volume. A comparison with the data for pure PIM-1 shows that the introduction of ZIF-8 particles in any concentration into the PIM-1 matrix results in an increase in the τ_4 lifetime, which characterizes larger holes. According to Tao-Eldrup formula the mean radius of free volume elements in PIM-1/ZIF-8 MMMs of 5.35 ˚A is slightly larger than that in neat PIM-1. More correct measurements in nitrogen atmosphere showed some increase in τ_4 upon addition of ZIF-8 to PIM-1, while the lifetimes are independent of the ZIF-8 content. In the case of PIM-EATB, the PALS method showed that the lifetime τ_4 is somewhat smaller than in PIM-1 in agreement with lower permeability of this polymer.

1.3.4.2 Pure gas and vapour permeation

The team of ITM was most intensively involved in the determination of gas and vapour transport properties of the membrane samples prepared by different partners of the consortium. Measurements were carried out at the fast-responding time lag apparatus, so that the contribution of both diffusion and solubility terms to the permeability could be determined for six permanent gases and several vapours, both in the neat polymers and in the MMMs. The transport properties measured through these membranes were also monitored over time to check the stability of these nanocomposite systems. Many of the nanoparticles with large BET surface areas, belonging to the classes of zeolites, metal organic frameworks, organic-cages and carbon nanotubes, were found to improve the already interesting transport properties of the original polymers, enhancing gas permeability for a number of important gas pairs (O_2/N_2; H_2/N_2, H_2/CH_4 and H_2/CO_2) over time. In some cases also the stability over time was improved, by reduction of the effects of physical aging in the presence of nanofiller particles.

1.3.4.3 Gas separation and mixed gas/vapour permeation

Studies of mixed gas permeation in dense films of different Si-containing tricyclononene polymers were conducted in TIPS for binary CH_4-C_4H_{10} mixtures, using gaschromatographic analysis of the gas composition. Such mixtures are often used in studies of highly permeable polymers with solubility controlled permeation. In order to study a mixture that better models associated petroleum gas, four-component mixture was investigated. The mixed gas data are compared with results of the individual gas permeation (upstream pressure 1 bar, pressure drop Δp=1 bar). The same trend of variation of the P values of alkanes is observed for pure gas and mixed C_1/C_4 gas permeation. A comparison of the results obtained for 2-and 4-components mixtures show the same observations. Permeability coefficient of methane in both mixtures is much lower than that in individual permeation of CH_4. It can be explained by blocking of pores in membranes by condensable component (C_4H_{10}). Such explanation was given in the studies of hydrocarbon permeation in polyacetylenes (Auvil, Pinnau). Permeability coefficients of butane in mixture permeation are also smaller than the pure C_4 permeability measured at 1 atm. It can be explained by concentration dependence of $P(C_4)$ what was confirmed experimentally.
Permeability coefficients of mixed gas permeation can be increased after treatment of the film with ethanol, as has been observed for individual gases and binary mixture. Since permeability coefficients of higher hydrocarbons (n-butane) are concentration (pressure) dependent, their values are sensitive not only to upstream but also to downstream pressure. It was confirmed by experiments where no He sweep was used, so the downstream pressure was 1 bar. With no He sweep (with higher concentrations of penetrants in the downstream side of membrane) permeability coefficients decrease while separation factors increase. The results indicate that Si-containing poly(tricyclononene)s exhibit solubility controlled permeation behaviour in separation of mixtures and not only in the experiments with pure gases, allowing enrichment of butane from associated petroleum gas: the concentration of butane in the permeate can be five-fold larger than in the feed stream. On the other hand, enrichment of ethane and propane is rather modest. It opens possibilities of using these materials for separation of hydrocarbons of natural and associated petroleum gases.

Another mixture of interest in this project was CO_2/N_2. The same phenomena were observed for the CO_2/N_2 (70/30 v/v) separation in PIM-1 + 40 wt.% of nano HKUST. A strong decrease in permeability of "slow" component (N_2) as compared with its P as pure gas and concentration dependence of $P(CO_2)$. Mixed gas separation factors $\alpha(CO_2/N_2)$=33.8 were significantly larger than ideal separation factor (22.6). These mixed matrix membranes also show solubility controlled permeation and are suitable for separation of the mixture containing highly sorbed components.

Different instrumental methods were used for the permeation measurements. At ICT, gas and vapor permeation experiments were performed at 25°C by a differential flow permeation apparatus[12,9] with H_2 as carrier gas. The temperature-controlled permeation cell inside the apparatus was partitioned by a flat circular membrane specimen, with a constant gas or H_2+vapor flux on the feed-

side and with pure H_2 flux on the permeate-side. The pressure on both membrane sides was identical. Measurements were carried out at atmospheric pressure (gases) or at different values of vapor saturations, ranging from 10 to 90% with respect to each tested vapor pressure at given temperature. From changes of thermal conductivity (pure H_2 vs. mixture of carrier gas and penetrant) the permeability coefficients were evaluated from the steady-state data. Diffusion coefficients were calculated from transient data.
In the case of binary vapor permeation (water and linear C_1-C_4 alcohols), the GC-MS device was used for the determination of the mixture composition.[12] First component in mixture was kept constant at a selected vapor saturation (activity) while saturation of the second component was varied. Such technique enables to reveal mutual (coupling) effects between components of studied mixtures of ROH^1-ROH^2 and ROH-H_2O. For instance, in the case of SBS membranes, the presence of second component in mixture positively influenced butanol flux, but reciprocally for ethanol the effect was negative or negligible. For water vapor, increasing butanol saturation increased the water permeation. These findings are related to solubility-controlled transport of vapors in SBS because butanol is the highly sorbing species and water sorption is nearly 10 times lower. Results obtained for PIM-1 revealed strong negative coupling effect of alcohols on concurrently permeating water vapor and such effect decreased water permeation rate. In ROH^1-ROH^2 systems the negative coupling effect was determined as wel. The only exception was for methanol-ethanol, where addition of methanol (with saturation 20, 40 and 60%) into ethanol resulted in 5 times higher ethanol flux than pure ethanol permeation.
A new model for anomalous vapor permeation through polymers (*e.g.*, PIM-1, Figure 1.7.) was created based on the irreversible thermodynamics approach on anomalous diffusion and sorption of vapors in solid films.[10] Laplace transform was used for solving the appropriate diffusion equations. The model implements a diffusion coefficient as a function of two variables: time t and a relaxation parameter β (Figure 1.7.).

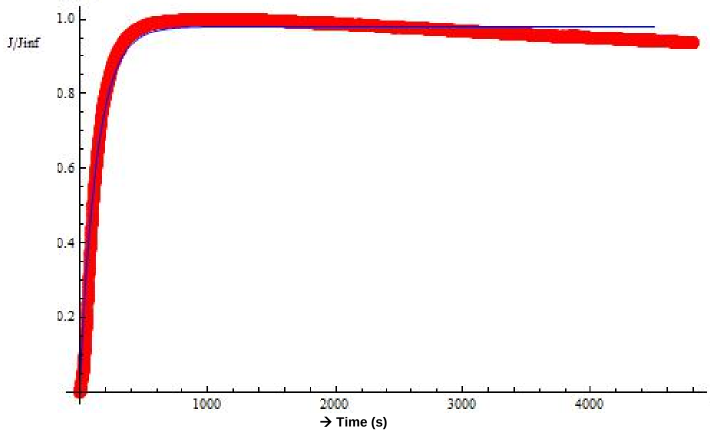


Figure 1.7. Comparison of created model (blue) with experimental values (red – normalised flux) of methanol vapor (activity a = 0.2) permeation through a PIM-1 membrane.

1.3.4.4 Sorption analysis

The basic transport phenomena were further analyzed at ICT by sorption measurements of gases, vapors or liquids. From the obtained data the permeability P, diffusion D and sorption S coefficients, connected in the solution-diffusion model for non-porous dense polymer matrix as $P = D \cdot S$, were evaluated.
Gas and vapor sorption experiments in flat membranes or in powder nanofillers (measured using aluminium holder) were performed at temperature 25°C using two self-developed sorption apparatuses equipped with a calibrated McBain quartz spiral balance and with an automatic CCD camera system detection of sample-target-point position.[11,12] D coefficients were evaluated from sorption kinetics, while S coefficients were obtained from equilibrium sorption values.

A novel method of filtering and smoothing of raw gravimetric sorption kinetics data of gases and vapors was developed because at the beginning of sorption experiment, introduction of sorbent from the pressure reservoir into the evacuated measuring chamber leads to spurious oscillations of the spiral balance. Such oscillations overlap with the real elongation of the spiral caused by gas/vapor sorption into a polymer membrane or nanofiller powder. Therefore, filtering out of such phenomena is necessary for evaluation of accurate values of the diffusion coefficients.
Liquid sorption experiments were performed gravimetrically with the procedure described in details.[11]

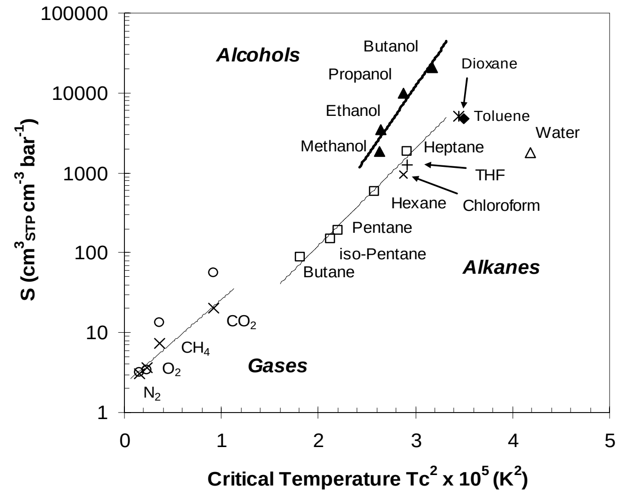


Figure 1.8. Correlation of sorption coefficient in PIM-1 with the square of critical temperature. Gas pressure 1 bar; vapors: activity $a = 0.67$ [13]

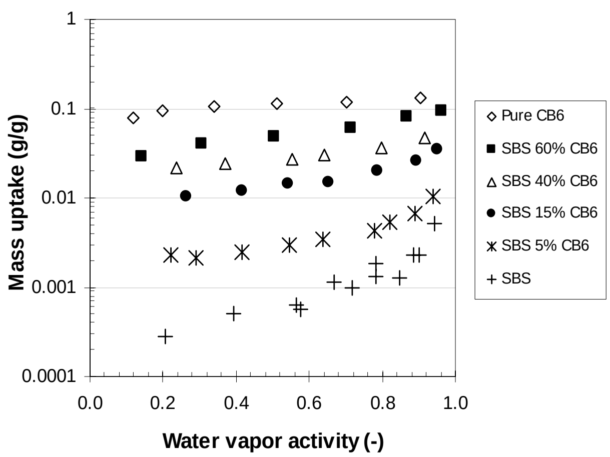
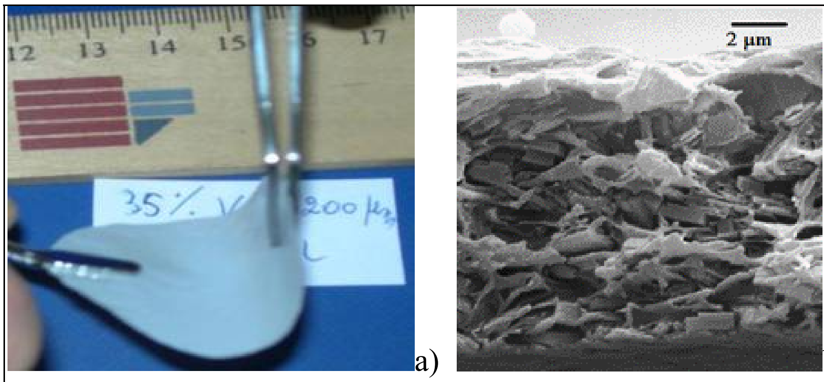


Figure 1.9. The effect of hydrophilic nanofiller cucurbit[6]uril (CB6) on water vapor sorption at 25°C in hydrophobic SBS based samples.

Different sets of MMMs for gas separation and ethanol/water pervaporation based on PIM-1 (UniMan), Hyflon AD60X, Teflon AF, poly(tricyclonorbornene-2Si) (PTCN-2Si, TIPS), poly(styrene-*b*-butadiene-*b*-styrene) (SBS), and containing the inorganic fillers of Table 1.1 were prepared and tested in gas permeation experiments by Unical.
Flexible and defect-free symmetric MMMs based on perfluorinated polymers can be prepared with a filler content of up to 44 volume percent (Figure 1.10. a). When SAPO-34 is used as a filler, an increase of both the ideal CO_2/CH_4 selectivity and the CO_2 permeability is observed with respect to the polymers. A CO_2/CH_4 selectivity up to 40 (+ 80%) was measured with Hyflon AD60X/SAPO-34 MMMs containing oriented high aspect ratio crystals (Figure 1.10. b). The use of both permeable and impermeable SAPO-34 as a filler indicated that the pore network of the latter gives a determining contribution to the overall transport. If we consider that Hyflon AD60X can withstand high partial pressures of CO_2 and of condensable hydrocarbons, these MMMs represent a viable alternative to the commercial membranes used today (polyimides and cellulose acetate) to "sweeten" natural gas with large amounts of acid gases.
Innovative SBS MMMs containing amino-modified mesoporous SBA-15-NH_2 – demonstrate improved CH_4/N_2 and CO_2/N_2 selectivity (7.3 and 53) and permeability (24 and 173 Barrer) with respect to SBS membranes prepared in the same fashion. SBS MMMs containing amino-modified[14] MCM-41-NH_2 gave CH_4/N_2 selectivity in excess of 8 with the same methane permeability.
The gas sorption isotherms on the as-made and on the modified fillers indicate that the amino groups decrease the pore volume and hence the sorption capacity of N_2, but leave almost unchanged the sorption capacity of CO_2 and of CH_4.
In addition to this, AFM (Figure 1.11.) and TEM analysis indicate that the aminated fillers induce the formation in SBS of hexagonal arrays of aligned polystyrene columns in a polybutadiene matrix, which in turn favor the swelling of the polymer and enhance the sorption selectivity, as

already observed in the literature for SBS membranes.[15] Thanks to the combination of high CH_4/N_2 and CO_2/N_2 ideal selectivity and permeability, these membranes can be used for the exploitation of natural gas wells containing high amounts of inert nitrogen, and for the CO_2 post-combustion capture.

The gas permeation measurements of SBS MMMs containing 2 wt% CNT-C18 (from ITM, Padua) show an unchanged permeability, but larger CH_4/N_2 and CO_2/N_2 selectivity (5.5 and 33) with respect to the neat polymer, probably an effect of the good compatibility between SBS and the modified polymer.



a) b)

Figure 1.10. Hyflon AD60X MMMs. a) Sample containing 35 v% of 0.2 µm SAPO-34, bent to show its flexibility. b) SEM image of the cross section of a sample containing 35 v% of oriented, 1.5 µm SAPO-34 crystals with aspect ratio 9.

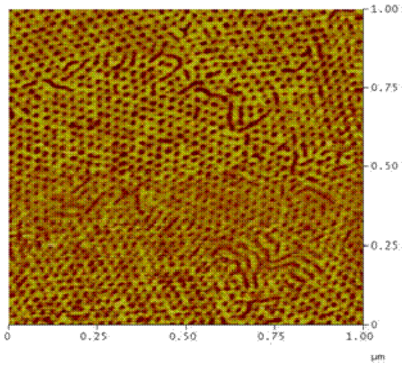


Figure 1.11. AFM image of the bottom layer of a SBS MMM containing 10 wt% SBA-15-NH_2.

1.3.4.5 Pervaporation

Defect-free MMMs for pervaporation (PV) based on PIM-1 or SBS, filled with silicalite-1 (MFI), showed in both systems that the presence of functionalized MFI crystals is able to increase the ethanol/water separation factor of the polymer: from 3.6 to 5.4 for SBS, and from 3.6 to 5.7 for PIM-1. With the highest MFI content (35 v%). In gas separation, a CO_2/N_2 selectivity of 30 was observed, beyond the value of PIM-1.

Membrane modules based on thin film composite SBS membranes, prepared by Vladipor, were successfully tested for pervaporation of ethanol/water mixtures. Whereas the membranes with polyurethane intermediate layer showed the highest gas selectivity, in pervaporation the membranes with silicone intermediate layer proved more selective, thanks to the hydrophobic character of the silicone.

1.3.5 Modelling studies

Modelling of the interaction between the membrane constituents and the permeants were studied at quantum mechanical level by ITM. Modelling of the structural and transport properties were further studied at ITM by atomistic or molecular modelling. On the other hand, Unical and KUL performed macroscopic modelling of the transport, both for the neat dense polymers and for the MMMs.

1.3.5.1 Modelling of neat polymer membranes

Computational methods were used at ITM to support and complement the experimental work.

Quantum Mechanical (QM) modelling was dedicated to the building of carbon nanotubes (CNTs) with the aim to select the functional group giving the most efficient interaction with CO_2 molecules.

Different functional groups have been anchored to the opening of the CNT. The separation based on specific non covalent interactions between gaseous molecules (CO_2, CH_4, N_2, O_2, H_2) and functionalized CNTs were considered. QM work has concluded that the length of the linkers does not affect the non-covalent bond between the heads and the CO_2, that the binding energies related to the bond between a functional group anchored and CO_2 is not affected significantly by other near functional group. Among eighteen heads examined, the chemical groups showing the most efficient adsorption of CO_2 (CO_2-phile) are amide groups, and finally the use of oligo ethylene glycol legs consisting of one monomer, minimum, avoids the blockage of CNT openings by the polymer chains that may completely eliminate the function of the CNTs embedded in the polymeric membranes. Then the evaluation of the interaction energies among the selected functional groups (CO_2-philic groups) of CNTs embedded in polymer membranes and the CO_2 molecules and to the configurational analysis of the functional groups to understand if their steric hindrance can discriminate the diffusion direction of CO_2 molecules.

The interaction of PIM-1 with water and lower alcohols was also studied using FTIR spectroscopy and quantum chemical calculations. The calculations showed that energetically most favourable water associate consists of 5 H_2O molecules; on the other hand, the most favourable associate of ethanol is a tetramer. Water associates are capable to form sufficiently strong bonds with oxygen atoms of both polymer chains, leading to a reduction of the size of microcavity to 9.6-8.7 Å. Single molecules of ethanol form relatively weaker hydrogen bonds, and this process is accompanied by increase of the size of microcavity to 12.5 Å. Weakly bonded alcohol can be easily desorbed at room temperature leaving larger holes inside the polymer, while water associates require heating above $100^{o}C$ for their removal. The latter explains why water has a negative effect on the permeability of PIM films.

Atomistic modelling activities considered the simulation of two PIM-polyimides, i.e., PIM-PI-1 and PIM-PI-8 and a new PIM-modified polymer with ethanoantracene units, PIM-TB. The amorphous polymer packings were prepared and several ns of MD simulations were performed. Free volume analysis and transport properties of gaseous species in the membrane materials have been evaluated. The solubility and diffusivity coefficients of H_2, O_2, N_2, CO_2, CH_4 have been calculated by using the Transition State Theory. Diffusion coefficients of gas molecules inserted in the models have also been calculated by MD analysis. Grand canonical Monte Carlo (GCMC) simulations of sorption isotherms have been carried out. The Free Volume distributions analysis was performed by using *Vconnect* and *Rmax* calculation methods by Hofmann. The theoretical values compared with experimental transport are in good agreement and provide useful structure-properties relationships.

Mass-transport through dense membranes in pervaporation was modeled by KUL. It can be described by three consecutive steps i.e.: sorption of components in the membrane, diffusion through the membrane and desorption from the membrane as a vapor into the permeate. While during sorption and desorption thermodynamic aspects are involved, diffusion is based on kinetic aspects. In hydrophobic pervaporation, the organic (here ethanol) is removed from the feed and upconcentrated in the permeate (which will be further treated by distillation), this at the expense of water. Since water is one of the smallest molecules in chemistry, diffusion characteristics for ethanol are not very favorable. Hence the sorption step will be the more dominant step towards the overall separation and therefore requires an accurate description. This description is often performed by the mass-based UNIQUAC model, since this standard very accurate thermodynamic model can be extended to polymer (membrane) systems. However, based on a deeper study, it was found that the currently used mass-based model is incorrect since the conversion from molar-based to mass based parameters has been performed erroneously.[16] This even leads to an incorrect description of simple vapor/liquid equilibrium. Since this forms the starting point for modeling sorption equilibrium in dense membranes, a correct outcome is unlikely, since the calculated activities are not based on correct thermodynamics. First, a correct and straightforward conversion from molar to mass based parameters could be provided, so that both models now give the same results for vapor/liquid equilibrium. Although the model makes use of specific UNIQUAC parameters, these are often large for membranes and difficult to determine. However, in the UNIQUAC equations, only ratios of these parameters are present which are demonstrated to be fairly fixed. Despite the fact that the more information is known about the membrane, the more accurate these ratios can be estimated, also with no membrane information a good estimate can be made. The use of these ratios was validated based on experimentally determined UNIQUAC parameters of membranes which matched almost perfectly with far less effort. Model calculations with these improved equations were found to be very accurate, and this even for very non-ideal polar mixtures.

1.3.5.2 Modelling of mixed matrix membranes

Mixed-matrix membranes consist of a continuous phase (polymer) and in general a randomly distributed disperse phase (filler). Therefore, the Maxwell model which is based on treatment of the conductivity of a dilute suspension of spheres was proposed next to the Cussler model which considers a staggered array of high aspect ratio particles. In this approach, the overall permeability is estimated based on the permeabilities in the pure polymer and pure filler, with additional information about the volume fraction and aspect ratio of the fillers. Permeabilities in pure polymer and filler are determined by adjusting experimental data to the Maxwell-Stefan equations. The effectiveness of both models was evaluated at KUL by comparing their predictions to two-dimensional finite element calculations for membranes of various geometries. Subsequently, the modified Cussler model was used to predict the separation performance of normal and iso-butane by Si-filled PTMSP membranes.[17] A theoretically obtained selectivity was of 15.6, while experimental data revealed a selectivity of only 5. This large discrepancy can be explained by the theoretical approach of both models which do not take into account some apparently decisive factors (interface phenomena). Although this approach is not suitable for absolute membrane performance prediction, it does provide some interesting insights for membrane designers (‘what-if’ cases). Finally, it was found that simple models like the standard solution-diffusion model do provide high descriptive accuracy. A model that is solely predictive has yet to be developed, but seems very difficult.

The gas permeability data of MMMs containing 20 and 35 vol.% of permeable and impermeable SAPO-34 of different size and shape have been used by Unical in the macroscopic modeling of the transport of gas based on the application of the Maxwell and the Cussler models. It was aimed at recognizing the presence and understanding the role of the basic phenomena governing the transport in MMMs: besides the permeability in the polymer bulk and in the filler, these are the alteration of the polymeric free volume next to the filler surface, and the barrier to transport on the outer surface of the porous filler particles. The modelling work clarified the single phenomena during the gas permeation process and has demonstrated that *i*) the Maxwell and the Cussler models alone are not able to describe the gas transport in MMMs; *ii*) the perfluoropolymer free volume increases at the interface with the porous filler; *iii*) a barrier for the transport of mass exists on the outer surface of the porous filler particles; and *iv*) the overall behaviour of the MMMs is determined by the specific interplay of the single basic effects. The situation of an amorphous and glassy perfluoropolymer/molecular sieve MMM is schematically depicted in Figure 1.12..

The presence of a barrier for the transport of mass at the surface of the molecular sieve may originate from the plugging of the pores by the polymer chains, by the surface modification of the filler, or by a different mechanism. Theoretical studies[18] indicate that the transport of mass through from the outside into a molecular sieve takes place in two steps: sorption onto the surface, and diffusion into the pore network. In order to verify experimentally this situation, the surface of large silicalite-1 (MFI) crystals (about 20 μm) was modified with four different alkyl groups, and the two experiments were carried out on them: H_2 sorption kinetics at 77 K, and Thermal Desorption spectroscopy (TDS) of H_2. The analysis of the H_2 sorption kinetics indicate that the diffusion rate inside the crystals is a function of the chemical nature of the outer surface, therefore a surface barrier for the transport of mass exists even on the surface of isolated crystals. The second important and surprising information is that, both in H_2 sorption kinetics at 77 K and in TDS experiments, the slowest diffusion takes place in the as-made MFI crystals, notwithstanding the bulky groups grafted on the modified MFI.

Figure 1.12. Schematic representation of the different regions in a MMM containing porous molecular sieves (yellow) in an amorphous and glassy perfluoropolymer matrix (blue). The light blue area around the molecular sieve represents a shell of higher free volume polymer, and the black line represents the barrier for the transport of mass on the outer surface of the porous filler particles.

The experimental evidence gathered for the MMMs based on perfluoropolymers raises a fundamental question: is it possible to extend the same conclusions to MMMs based on other glassy or rubbery polymers? If the answer is yes, to which extent? Is the barrier to transport on the outer surface of molecular sieves just a problem, or a new opportunity? In any case there is ground for new investigations.

1.3.6 Application tests and demonstrations.

While the core of the DoubleNanoMem project was focused on materials science aspects of new membrane materials, there was also a strong accent on applied research to evaluate the practical potential of the novel materials. The two industrial partners have a strong focus on applied research, Vladipor in membrane production and TPI in the use of membrane technology for gas separations. Also the TUD and KUL have a strong tradition in applied research, in the context of DoubleNanoMem especially related to pervaporation.

1.3.6.1 Applied pervaporation

Influence of fermentation by-products on the membrane performance during pervaporation
Research at KUL showed that although ethanol and water are the main components in the fermentation broth that must be purified to fuel grade ethanol, other by-products can be present which could hinder the subsequent purification. These can be subdivided into metabolic secreted by-products during fermentation and by-products formed during the acidic pre-treatment step. The influence on the membrane performance of the former group has been extensively investigated.[19] On one hand, no significant and irreversible effects were observed on commercially used pure polydimethylsiloxane (PDMS) membranes. On the other hand, severe membrane fouling was observed on a silicalite-1 filled PDMS membrane. These mixed matrix membranes (MMMs) are very promising and hence deserve more attention than the pure polymeric membranes. The reason of the membrane fouling was the interaction of carboxylic acids in the fermentation broth with silanol end-groups of the zeolite particles. Ester bonds were formed, which rendered the membrane more hydrophilic and hence decrease the membrane's ethanol selectivity. This was confirmed by water contact angle measurements which revealed a significant decrease in water contact angle of

the zeolite filled membrane. No cleaning methods were found to be suitable in order to restore the original membrane properties. It was furthermore found that by increasing the pH towards more neutral environments (from 3 to 6-7), membrane fouling completely diminished. This could be explained by the fact that dissociated weak acids, which are mainly present above their dissociation constant, show almost no affinity and hence interaction with zeolite particles. Hence, the focus must go towards either developing microorganisms that produce ethanol at more neutral pH or a proper filler modification that replaces the reactive silanol end-groups of the zeolites.

Once optimized materials have been found, a complete process for bioethanol production must consist of the fermentation unit as well as the downstream processing section. In this project membrane operations for the ethanol purification were studied and process was analyzed both experimentally and by modelling.

Modelling of an integrated fermentation-pervaporation system
In the evaluations of TUD, the two-stage fermenter coupled with pervaporation was selected as a model system (Figure 1.13.) and the goal was to evaluate this system numerically, experimentally and economically. To investigate the performance of integrated system, modelling was done by using Matlab. The integrated model consists of fermentation and pervaporation model. In the fermentation model, the separation of aerobic (growth) and anaerobic (ethanol production) fermentation was done on the basis of stoichiometric equations of *S. cerevisiae* in respective fermentation modes. The effect of dilution rates, recycle flow ratio, recycle from stage 2 to 1, on the concentration profiles in both fermenter and ethanol concentration in permeate from pervaporation were examined in this model. The pervaporation model mainly includes the flux calculation and determination of permeate ethanol concentration from selectivity of the membrane. The effect of variation in selectivity on membrane flux and ethanol concentration, and ethanol fraction in feed and permeate was also evaluated.

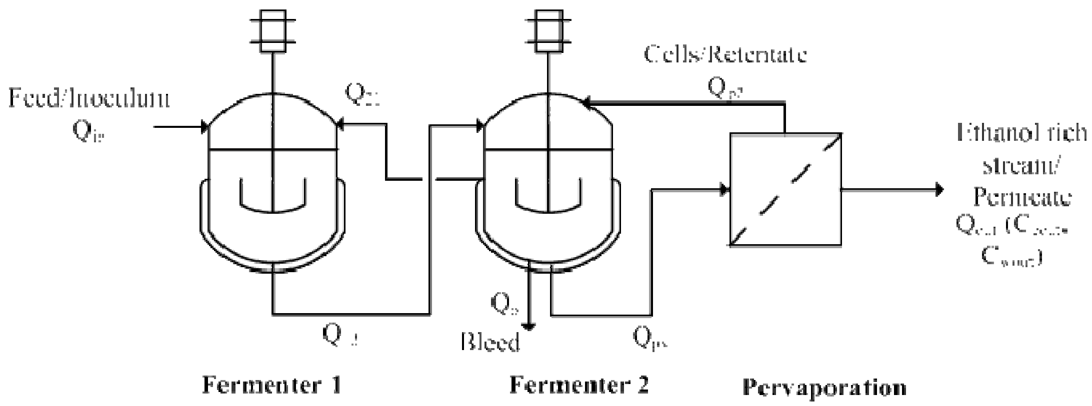


Figure 1.13. Schematic diagram of the model integrated membrane system.

During the preliminary experiment with integrated system, the ethanol formation in aerobic phase and biomass production in anaerobic phase was observed. The metabolic reaction model, which includes this phenomenon, was build-up. But, it still needs to be modified and updated. Also, model based optimization of process parameters (dilution rate, recycle flow rates, feed concentration) for continuous two stage fermenter system on the basis of experimental results and reconciliation of data (data fitting) will be done in future. The work is still in progress.

Experimental analysis of integrated system
An integration experiment was performed successfully by coupling the two systems. The yeast strain *Saccharomyces cerevisiae* CEN.PK 113 7D was used during this integration experiment. The

batch phase started at same time in both fermenters with continuous air flow. The cell cultivation was carried out at by a precise experimental protocol. When the fermentation system reached the steady state, the appropriately sterilized pervaporation system was integrated. The fermentation broth was circulated through feed side, maintaining the permeate pressure at 10 mbar. The retentate was sent back to the fermenter and the permeate was collected in flasks kept in cryostats with temperature of -10 ^{o}C. Commercially available PDMS membranes were used for the initial studies.
During the integrated experiment, severe fouling of the PV membrane based on PDMS was observed. Potential candidates for membrane fouling that were identified by KUL (see above) and were cellular polymers such as lipids, proteins, polysaccharides and nucleic acids. The model components for these cellular polymers (Table 1.3) were evaluated for the PDMS and POMS membrane fouling.

Table 1.3. Types of representative synthetic cellular polymers investigated.

Cellular polymer	Represented by
Proteins	BSA
	Lysozyme
Lipids (triglyceride)	Glyceryl trioleate
Phospholipid	1,2 dipalmitoyl-sn-glycero-3-phosphocholine
RNA	RNA from *Torula* yeast
Polysaccharides	Glycogen from bovine liver

The performance of both membranes dropped severely in the presence of lipids. The hydrophobic interaction between membrane and lipids resulting in higher adsorption of lipids might be the cause of this fouling. Proteins were observed to be the next most important fouling component in PDMS.The total flux in PDMS decreased with increasing BSA concentration whereas lysozyme did not affect the membrane. Also, the effects of glycogen and RNA on PDMS membrane were insignificant. The selectivity of PDMS membrane remained unchanged during these experiments because the extent of decrease was the same for total fluxes and partial fluxes. POMS membranes, being more hydrophobic than PDMS, were found to be more susceptible to fouling for all bio-polymers. The POMS membrane selctivity was not altered by these polymers. The detailed results can be found in a published paper.[20]

Pervaporation of lignocellulosic fermentation broth components
The effects of lignocellulosic fermentation by-products on PDMS membrane performance for the recovery of ethanol by pervaporation was investigated. The performance of the membrane was evaluated in presence of real fermentation broths and selected model components.
Three types of fermentation broths, based on different feedstocks and pretreatment method, were obtained from TNO (Table 1.4).

Table 1.4. Ligno-cellulosic fermentation broth. Source: TNO, Zeist.

Broth	Biomass	Pre-treatment method	Ethanol conc. (g/L)
F9	Barley straw	Concentrated acid	21.7
F12	Willow wood chips	Mild alkaline	8.7
F13	Barley straw	Mild alkaline	13.3

The make-up of the ethanol was done, before performing PV experiment, so as to have final ethanol concentration of 3 wt.%. The results obtained showed that the membrane performance decreases, compared to base case, by all the fermentation broths. A total flux decrease up to 20% was found with the different broth types. The water flux suffers more than ethanol flux in all cases, resulting in

higher selectivities than in the respective base case and regeneration experiments. For all fermentation broths tested, the membrane fouling was irreversible.
The common components present in the lignocellulosic fermentation broth were derived from the literature. These components were also identified in tested broths. For the ease of experiment and comparison, PV experiments were carried out with 1 g/L of each component in 3 wt.% ethanol-water solution. The results obtained with individual model components showed that vanillin, 4-hydorxy benzaldehyde, catechol and syringaldehyde foul the membrane and decreases the total flux by 12-15%. Also, furfural permeates through the membrane and increases the total flux. The percentage decrease in the flux observed by using actual fermentation broth was in the same range as that obtained using the model components, supporting the hypothesis that the tested model components, also found in the broths, are responsible for the membrane fouling.

Ethanol stripping by CO_2 and ethanol recovery by vapor permeation
The fouling of the pervaporation membrane caused by fermentation by-products could limit its industrial application. To avoid this fouling, different process options have been suggested in literature. Here we propose the stripping of ethanol by using CO_2 and ethanol separation by vapour permeation. This process can also be applied to recover ethanol from fermenter off-gas. Thus the aim of this study was to investigate the applicability of vapour permeation for ethanol recovery from fermenter by CO_2 stripping and from fermenter off-gas. The prerequisite for this process to be applicable is the availability of membranes capable of separating ethanol from CO_2. This subject of further studies beyond the duration of the DoubleNanoMem project.

Preliminary cost analysis
In order to be economically viable, the novel process must be able to compete with currently available techniques, not only in performance but also in total process costs. An estimation of the cost was made by KUL and TUD for two different systems.

Bio-ethanol purification by a hybrid pervaporation-distillation section
Since one of the aims of the project was the intensification of bio-ethanol production by altering the purification section, the current absolute production cost must first be determined. A discounted cash flow analysis was performed based on a techno-economic model of a lignocellulosic ethanol refinery. It was found that for the base case were a two step distillation, followed by molecular sieve adsorption is used for purification, the ethanol production cost is \$651 per m^3 ethanol. It was furthermore found that the purification sections accounts for less than 7% of the total production cost and for less than 13% of the total electricity consumption of the plant. A second case was investigated, where the first distillation column was replaced by a pervaporation (PV) unit, since this hybrid setup has advantages over the conventional technique. Based on the performance specifications of currently synthesizable membranes, it was found that the absolute production cost would increase by 3%, which was mainly due to an almost 3-fold higher capital investment cost of the purification section. Although the net electricity requirements decreased only marginally, lower steam consumption was observed in purification section and hence, more excess electricity could be produced in the second case. This excess electricity is probably the most decisive factors of lignocellulosic ethanol and therefore of utter importance. Finally, it was found that a flux increase rather than an increase in selectivity will significantly decrease the production cost of ethanol. Hence, for this application the focus for membrane producers should be on a drastic increase of the flux, thereby maintaining a moderately high (but not excessive) ethanol selectivity (α of 10 to 12).

A complete process and economic model, to analyse the feasibility of implementing PV as an alternative to distillation in the production of bio-ethanol, has been developed by TUD using MATLAB R2010a. A conceptual process designed by Kwiatkowski *et al.*[21] in SuperProDesign was used as the base case. This describes fermentative ethanol production with traditional recovery by distillation, at a scale of 150 million L/yr. The pervaporation unit was incorporated in the base case just by replacing the distillation. The costs obtained for distillation were deducted and the costs for pervaporation were included in the overall costs. The values for the PV costs and stream compositions were calculated off-line from the model developed as described above. An advantage of this approach is the accuracy. If this off-line pervaporation model simulation results in the same incoming and outgoing streams as that of distillation units, then it can be integrated with base case and perfectly accurate model can be obtained for the production of bio-ethanol. Also, if this new integrated model turns out to be economically feasible as compared to that with process containing distillation, then replacing the distillation by the PV unit will be sure a cheaper alternative.

1.3.6.2 Applied Gas separation

A macroscopic model for designing the membrane gas separation system was elaborated at ITM. It provides the performance of membrane units (e.g. purity level and recovery value, membrane area) to achieve the target separation using the experimental data obtained on the membrane materials developed during the project. The model uses the experimental data obtained on the membrane materials developed during the project and was applied to two different case studies, the biogas separation in which a stream composed of CH_4 and CO_2 has to be treated in order to remove the CO_2 leaving the methane at a high pressure and the flue gas separation in which a current of CO_2, N_2 and some O_2 is treated in order to avoid te CO_2 emission in the atmosphere. The use of membrane units in an integrated flue gas separation process plant was investigated in collaboration with TPI in order to take advantage of synergic action of different separation techniques. A separation system comprising a single membrane stage based on different composite membranes with a hypothetical selective layer of 1 micron and a solvent absorption unit was adopted considered. The membrane unit processes the cooled raw gas stream to enrich its CO_2 content, thus optimizing the performance of the next absorption unit. The hybrid system allows to save in the fixed and operating cost of the absorption unit but, the presence of the compressor that provides the driving force to membrane unit, slightly increases the total cost compared to a conventional absorption plant. More encouraging results were obtained in biogas treatment, where a system equipped with two membrane stages in series is capable to recover methane at the purity level required for its direct use in pipelines.

The task of the industrial partner TPI was to design and assemble a membrane gas separation pilot unit to test the modules developed by the consortium. Systems for CO_2 separation from nitrogen (flue gas from power plants and lime burning ovens) or for the sweetening of natural gas or biogas were evaluated. The test plant was optimized using commercially available modules with known performance. Because of the increasing interest on the biogas upgrading plants, tests were mainly focused on CH_4/CO_2 separation, the key separation of this process. The tests with commercial hollow fibre membrane modules showed a good and satisfactory CH_4 purity in the retentate, up to 98% vol. with a 2 stage membrane process.

A set of permeation tests was carried out at TPI in collaboration with ITM on the large size Pebax-based spiral wound module (5 m2) manufactured by Vladipor (Figure 1.14). A binary CO_2/CH_4 mixture, simulating a dry biogas stream, was used, giving CO_2/CH_4 selectivity values in the range of 12-15 at ca. 40°C, whereas a CO_2/CH_4 ideal selectivity of 20 was measured on flat sheet laboratory samples at ITM at room temperature. The CO_2 content was enriched from 60% in the feed stream to over 91% in the permeate stream and starting with a higher CO_2 feed concentration it is possible to overcome the CO_2 purity of 96% in the permeate stream under the appropriate conditions. In a second set of tests carried out by TPI with commercial modules, hydrocarbon mixtures were separated with the objective to enrich ethane. A two-stage process allowed to enrich

ethane concentration in the 2nd stage retentate from 27% to almost 50% (flowrate 150 L/min, pressure 2.8 bar).
A process model developed by ITM was used for two different case studies: *the biogas upgrading* in which CO_2 has to be removed from a stream composed of CH_4 and CO_2, while methane must remain at high pressure, and the *flue gas separation* in which a current of CO_2, N_2 and some O_2 is treated in order to avoid the CO_2 emission in the atmosphere.

Figure 1.14. V. Dzyubenko (Vladipor) with a large scale spiral-wound module with 5m^2 active surface (left), assembled for use in the TPI pilot plant in the blue housing (right).

A) Flue gas separation
A hybrid process scheme comprising a single membrane stage before the amine absorption unit was modelled. Different composite membranes with a 1 micron thick selective layer were considered. The materials considered were: PIM-1, PIM-1 after EtOH, PIM-1+CNT (15%) after MeOH, PIM-1+Cage3 (30%) after EtOH and Pebax®1657. The membranes based on PIM-1 were considered after an aging period of ca. 1 year. The membrane unit, processing the cooled raw gas stream, was used to enrich the CO_2 content from 13% to 30%, thus optimizing the performance of the next absorption unit. For the permeation of 100 Nm^3/h of CO_2 at 4 bar the required membrane area ranges from about 15 to 2500 m^2 for PIM-1-based MMMs and Pebax® 1657, respectively. Higher CO_2 purity levels are more easily achieved using the less permeable but more selective Pebax®1657 material.
The process design study and economic assessment by TPI for the hybrid process revealed that the hybrid solution is more expensive, both as plant cost (10% more) and as operating cost (doubled) compared with the traditional absorption technology. This is mainly due to the a very expensive compressor (or a vacuum system in the permeate), also in terms of energy requirements and maintenance costs. In this scheme CO_2 is recovered in the low-pressure stream and all the pressure generated by the compressor is wasted if CO_2 is the product to be recovered.

B) Biogas treatment
The application of the model to the CO_2/CH_4 separation in biogas treatment allows to evaluate the performance of a two-stage in series membrane unit according to the scheme adopted at TPI. For Pebax membranes the effect of the feed pressure on the CO_2 and CH_4 concentrations in the permeate and retentate streams exiting from the first membrane stage, is shown in Figure 1.15. As the permeate fraction increases (stage cut = permeate fraction of the feed stream), CO_2 fraction in the permeate stream decreases while CH_4 purity in the retentate high pressure side increases.

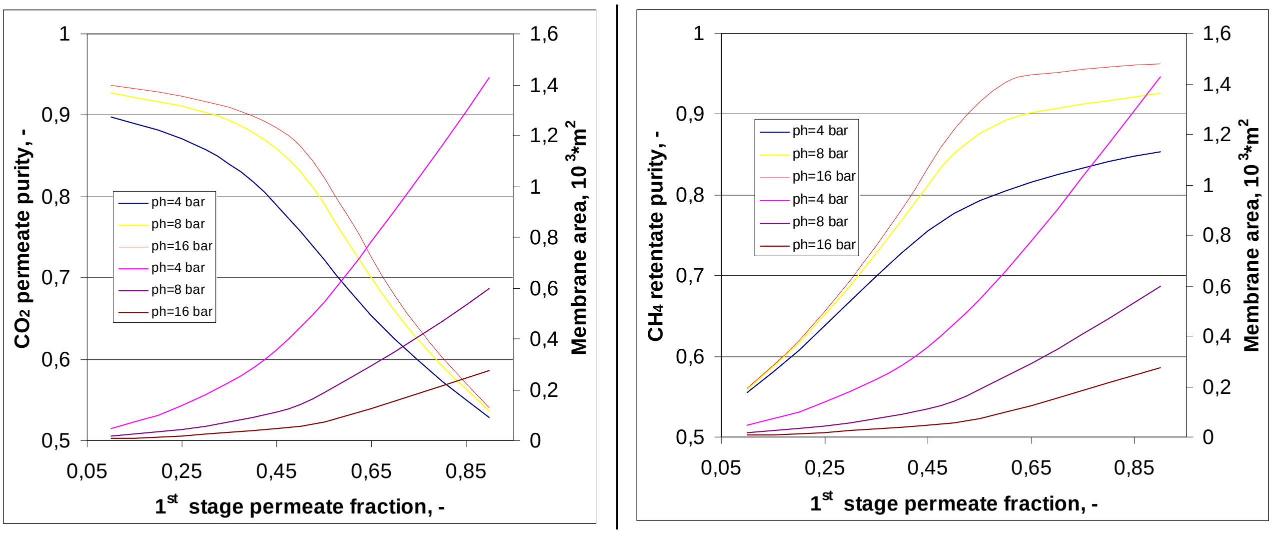


Figure 1.15. Pebax membrane system. Performance of the first stage. (a) CO_2 purity in the permeate and membrane area *vs*. stage cut. (b) CH_4 purity in the residue stream and membrane area *vs*. stage cut.

At the desired CH_4 purity of 98% for the high pressure retentate stream from the 2^{nd} membrane stage, a methane recovery of 60% was achieved operating at 16 bar, whereas it is only of 20% if the feed pressure is equal to 8 bar. In the last case, the required membrane area is also 4 times larger. A more permeable and equally selective membrane materials reduces the membrane area required at the same conditions in terms of methane purity and recovery.
Thus the most promising application of membrane processes is the biogas upgrading, that allows to obtain methane in the retentate at the purity required for its direct use or its injection into the methane grid TPI is further developing this application at industrial scale.
A small-scale bench-top CO_2 separation and analysis unit was designed for optimal testing of the modules produced in WP4 in an integrated membrane-based process and for evaluation of process cost. This task was carried out using the permeation experiments by TPI. The separation and analysis unit was constructed at the beginning of the project and it has been modified during the project in order to fit with the new modules tested and to adapt to the different mixtures separations and analysis needed. The plant is equipped with four mass flow meters for CH_4/CO_2, three CH_4 analyzers, five pressure transmitters, digital displays showing real time concentrations and a data-logger which register all the operating parameters (pressures, flows, temperature and concentrations) every five seconds. The target permeate flux around 1 m^2/h.

1.3.7 Project output

The project has been very productive from a scientific point of view, with one patent, more than 30 publications in peer-reviewed journals or book chapters and over 130 oral or poster presentations at international conferences and workshops. One international workshop and exhibition was organized even in the frame of the project. The last publications were accepted in very prestigious journals like *Angewandte Chemie*, *Advanced Materials* and *Science*.
Activities were further promoted at various international fairs and exhibitions, or in national events, demonstrations at the participating universities etc..
A number of the project teams continue their collaborations in at least 5 different formal collaborations.

1.4 Potential impact (including the socio-economic impact and the wider societal implications of the project so far) and the main dissemination activities and exploitation of results.

The DoubleNanoMem project was structured to be highly result-oriented with maximum interaction between the various activities, each accommodated in their own specific work package (Figure 1.16). It was set up with a strong scientific focus, especially on materials science and membrane transport phenomena, and a somewhat lower but fundamental effort on the final separation processes. The dissemination and exploitation workpackage guaranteed the maximum impact, which largely reflected the project structure itself.

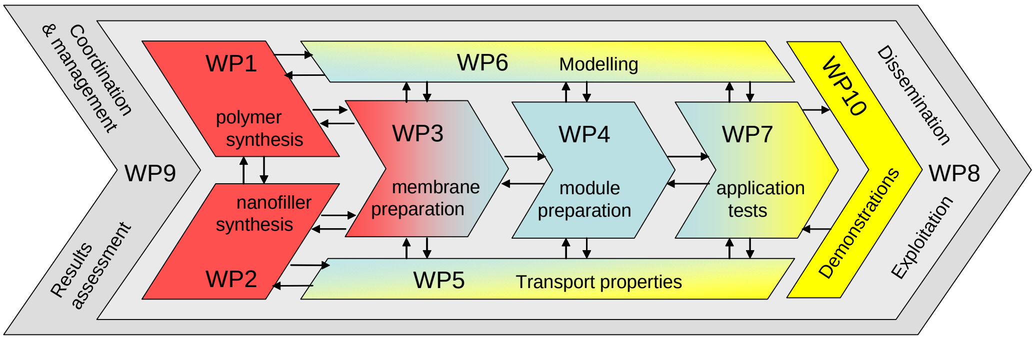


Figure 1.16. Highly integrated result-oriented project structure.

1.4.1 Scientific Impact

Given the project focus, the scientific impact is most evident in the project. This concerns roughly the following fields:

- Novel polymer and filler synthesis.
- Advances in membrane structure and transport properties.
- New insight in bioethanol pervaporation
- Progress in gas separation membranes and processes

While quantitative measurement of the impact may be difficult, at scientific level the number and the quality of the scientific publications and communications at international conferences is surely a valid indicator of the potential impact (see dissemination section below).

Novel polymer and filler synthesis. Great steps forward have been made in polymer synthesis. A totally new concept of polymerization by Tröger's base formation, giving an extremely stiff backbone, opened a new route to synthesis of novel polymers. Potential application fields extend far beyond membrane separations. The importance of this finding was clearly recognized by the scientific community, as can be evinced from the very recent acceptance of the related manuscript in *Science*. Earlier results on related polymer structures were already published in another High impact journal *Advanced Materials*. Besides the originally planned carbon nanotube and zeolitic fillers, attention has been more and more shifted during the project towards the metal organic frameworks and even to totally organic fillers. The latter are largely unexplored in relation to membranes and may have great potential. At the same time the potential of MOFs has clearly been recognized already and their development and application is now booming.

Advances in membrane structure and transport properties. Polymers of intrinsic microporosity as such are relatively new materials and many of their properties, also in relation to membrane performance, are still largely unexplored. New insight into the fundamental aspects determining their transport properties (permeability, solubility, diffusion), and development of new structure-property relationships has already lead in the project consortium itself to a gradual and systematic improvement of many materials, in several cases to values exceeding significantly the well.known Robeson Upper bound. Experimental work was supported by modelling studies and since the materials are in some cases completely unique, the modelling not only leads to better understanding of the materials properties, the use of consolidated techniques on novel polymers offers also a possibility to upgrade the computational methods.

New insight into bioethanol pervaporation. Development of fundamentally better membranes than the current state of the art membranes for pervaporation has proved to be an unreachable goal. From feasibility studies with membranes from the consortium and commercial membranes, it follows that in particular the selectivity of ethanol over water must be significantly be improved for PV to become a seriously interesting alternative for the traditional techniques for ethanol recovery from fermentation processes. The main out come of this part of the project is from the better understanding of fouling processes of the membranes when operating with pervaporation broth.

Gas separation processes. Although some small scale samples have proved extremely interesting for separation of particular gas couples, none of them was developed at sufficiently large scale to allow complete evaluation of the separation process under normal operation conditions. Simulations of the process, based on the performance indicators of laboratory scale samples shows nevertheless high potential of several of the novel materials.

1.4.2 Socio-economic impact and wider societal implications

The DoubleNanoMem project has tackled some of the most important global challenges that humanity encounters in XXI Century, related to energy and environment:

- Fighting the global warming caused by accelerating discharge of greenhouse gases such as carbon dioxide and methane into atmosphere, for a better climate.
- Finding alternatives to replace hydrocarbon based fossil fuels by alternative sources of energy such biofuel, for a sustainable future.
- Reducing the emission of undesirable pollutants (SO_2, H_2S, organic vapours) into atmosphere, for a healthier environment.

All these problems are interrelated and membrane technology, nowadays recognized as one of the most promising solutions for realizing process intensification, can help in solving many of these problems. Indeed, more and more membrane based processes are being developed in this area. In this light, the aim of the DoubleNanoMem project was to design and develop novel membranes with an improved combination of permeability and selectivity, that are better than the well know permeability-selectivity trade-off generally represented by the Robeson diagram. The mixed matrix approach proved to be successful with several polymer-filler combinations[22,23] and with newly designed pure polymers,[24,25] giving significantly better performance than current state of the art membranes defined by the Robeson upper bound. This work has been published in the most prestigious journals (Angewandte Chemie, Advanced Materials, Science), or has been covered by a European patent, which increases the prestige of European Research.
Realizing that significant improvement of membrane materials is apparently possible, one can imagine that upon further development of these materials the most direct impact of the project is the availability on the market of a new generation of membranes with greatly enhanced performance (selectivity, permeability, thermal resistance) compared to traditional polymeric membranes, This market is now dominated by overseas companies. It would also be a demonstration that membrane

technology will offer a valid alternative for traditional processes for *CO_2 separation in power stations* and other installations with even higher CO_2 emissions, such as lime ovens, thus reducing the carbon dioxide footprint of the processes involved.
So far, most results of the project are at research level, and although research itself does not have a direct impact on society, apart from the employment of the researchers involved, the importance of the research results has been recognized, as evidenced by the funding or approval of various national or bilateral projects to continue the research on the topics of the project (e.g. involving the teams of CU/ICT/ITM, the teams of ITM/Unical/TPI, the team of UniMan). These projects, as well as their results, are widely publicized, also to the general public, and the most direct societal impact in the increasing awareness about the problem of global warming, the potential solutions and ways to avoid it. This is strengthened by the association of the DoubleNanoMem project with the topics of the well-known *Kyoto Protocol*.
Another aspect to which the society is relatively sensitive is what to do with the permeate enriched with carbon dioxide. The presence of the industrial partner TPI, actually producer of CO_2 separation and production plants, introduces important market knowledge for CO_2 to the consortium. Although this subject was beyond the scope of this project, though several possibilities can be considered. One solution is employing of CO_2 in greenhouses for production of fruit and vegetables. Other uses are related to the beverage industry, where large amounts of CO_2 are used for gassed drinks, while there is also a considerable industrial use of CO_2 Some of these applications are based on incredible paradoxes, which should not exist in a society aiming at a sustainable future. For instance, the practice to use CO_2 in greenhouses is widely applied in The Netherlands, where normally the CO_2 is produced by their own heating system and then recycled into the greenhouse. Paradoxically during the summer period, when heating is not necessary, extra fuel is burned just for the CO_2 production. Furthermore, while millions of Euros are spent worldwide on research and practical implementation of *underground CO_2 storage*, at the same time there is still widespread production and use of *CO_2 from underground reserves* (e.g. Tuscany (Italy), Balcan area, several places in USA). Finally, in areas like the middle east, with large oil reserves and few other resources, much of the CO_2 need is covered by direct burning of gas or oil in a burner integrated with the CO_2 production plants.
The existence of such paradoxes is of course extremely discouraging for the common public if they are asked to make their contribution to a more environmentally friendly society. It is therefore of utmost importance that the CO_2 cycle is closed wherever possible. One step further can be made if the CO_2 could be used for growth of crops with subsequent application as biofuels.

1.4.3 Plan for the use and dissemination of foreground

Visibility and recognizability is one of the essential targets of the project. The specially designed logo (figure) has been used to identify the project throughout its entire duration. It represents a clean water stream coming from what can be interpreted at the same time as a tree, symbol of a vigorous nature, or as a 'green' cloud above a chimney, symbolizing sustainability of industrial production.
A special work package was dedicated to all dissemination activities, comprising also activities related to the exploitation of the project results and IPR management under the joint responsibility of the project coordinator Dr. J. Jansen, ITM-CNR's responsible for international relations, Ms. M. Liberti and Ing. U. Moretti of the industrial partner TecnoProject Industriale.

1.4.3.1 Dissemination

The dissemination plan is an essential part of the project's strategy to optimize its impact and its direct aim is to promote the exchange of knowledge and scientific excellence, to increase the public awareness and to pave the way for successful exploitation of the results. Within the project, dissemination is always given second highest priority in any activity of the project, after verifying of course that it does not adversely affect the possible protection of Intellectual Property or otherwise harm the interests of any of the partners.
Before any dissemination action could take place, the team leader of each consortium member was therefore informed about the dissemination intent and dissemination was only authorized if non of the beneficiaries made objections against it.

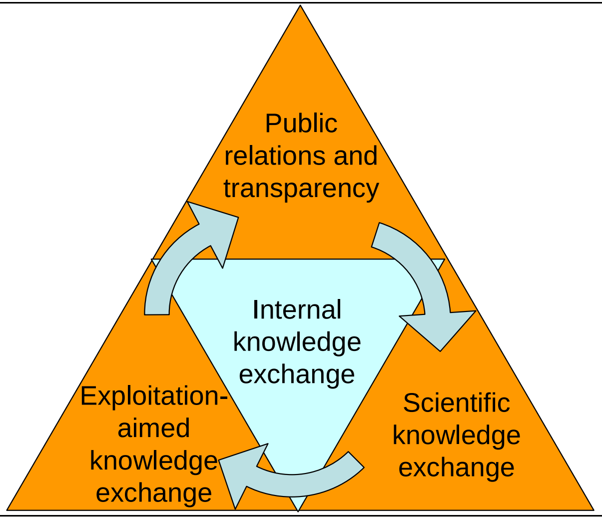


Figure 1.17. **Dissemination contexts of the project.**

Dissemination contexts

The dissemination takes place in four different contexts (Figure 1.17), each aimed at a specific target group, and all together aimed at maximization of the project's productivity, impact and visibility.

- *Internal dissemination* among the project partners, assures that all partners in the consortium are continuously informed about important developments in the project. Promoting the dialogue and the exchange of information is also the most crucial means to reinforce the coherence of the consortium, resulting in increased productivity and scientific excellence.
- *Public dissemination* of the generic project information, targets and achievements is part of a transparency policy to increase public awareness.
- *Dissemination of the scientific achievements of the project* promotes the results to a world-wide expert audience at conferences, workshops and through the scientific literature. It will stimulate open discussions and provide useful feedback from the international scientific community, raising the scientific standard of the project.
- *Finally, dissemination to a selected industrial target group* is aimed at the more successful exploitation of the project results, by increasing the awareness of their potential application.

Dissemination tools

A series of different tools has been activated and will be kept active to guarantee the most efficient dissemination of the project information and results, to begin with online facilities and internet.

A **dedicated web-site** (www.itm.cnr.it/doublenanomem) represents the main platform for information exchange to guarantee constant project visibility.
The web-site is structured in a **public access area**, where external visitors will have access to a brief project description, partners background, non-confidential data, as well as links to scientific publications. The scope of the public site is to raise the image of the project and to improve dissemination of the results and their possible applications to specialists, potential users of the developed technologies, as well as the general public.

A **restricted area** for project partners and the EC office provides access to internal reports and serves as a means to enhance internal information exchange.

Printed general information material has been developed as a more permanent and tangible form of documentation of facts and figures from the project. It has been distributed through direct channels, like through personal contacts of each partner, and at conferences and exhibitions. It is meant to increase visibility of the project also if people are not specifically looking for it. The planned printed information materials will remain accessible via the project website and comprises:

- A project brochure with the project information n a nutshell.
- An annual Newsletter, providing information about the state of the research, results, events within the project, and any other announcement of potential interest. During the project it has been advertised thanks to an e-mailing sent to every partner and through major events, such as conferences, exhibitions and workshops.
- Posters to be exposed in meetings, conferences and exhibitions of offer people an overview of the entire project “at a glance”.
- Press releases in the case of relevant events.
- Selected articles in existing newsletters of the individual institutes or for instance the European Membrane Society.
- Articles in popular-scientific journals for the general public.

Publications and presentations. Participation to national and international scientific events is the most important means in the dissemination strategy to promote scientific communication. The two main aims are to achieve European and world-wide visibility and to increase scientific quality through interaction with the rest of the scientific community. Publications in high-ranked Journals and presentation at the major international conferences permit to open discussions and receive useful feedback from the scientific community. The usual communication channels are exploited:

- Participation to targeted national and international scientific conferences, seminars, workshops, fairs to promote discussions and to receive feedback from the scientific community.
- Organization of a dedicated workshop/exhibition on the main research themes in the second half of the project.
- Publication of papers related to the project in the scientific literature will warrant the communication of the achieved results among the widest possible scientific audience.
- Integration of special topics of the project in undergraduate courses at each of the participating institutions.

In the course of the project, more than 30 manuscripts (publications, book chapters) have been submitted for publication in top-scientific journals, some of which still under evaluation or in the phase of revision. Given the young age of the manuscripts their impact in terms of the number of citations is still limited, but some manuscripts are showing significant interest even in the first year. Some statistics are given in the table below:

The last means to improve dissemination is via **short term staff exchange** and **coordination with other programmes** such as Erasmus exchange projects or bilateral national research projects was promoted to increase the internal dissemination, to improve the integration of the partners’ research activities and to stimulate the exchange of skills and results.
In total 12 permanent and temporary staff members were involved in staff exchanges of one week or longer and the total duration exceeded 14 person months. The exchange took place in the frame of the DoubleNanoMem project itself or in the frame of other programs, such as Erasmus projects or bilateral collaborative projects. Four persons were also involved in short term visits of one or several days. The total staff exchange involved twice the planned number of people and the total

duration of the exchanges was three times higher than planned, evidencing the very good interaction between the teams in the project. The latter could also be deduced from the extremely intense sample exchange and the number of joint publications.

Table 1.5. Impact of the manuscripts according to Scopus.

Manuscripts	Accepted	Under evaluation
	24	7
Indexation	Indexed in Scopus	Not yet indexed
	22 manuscripts + 2 abstracts	2 online + 2 in press manuscripts
Citations:	With auto-citations	Without auto-citations
2011	19	10
2012	33	22
total	52	32
h-factor	4	3

1.4.3.2 Exploitation of results

The exploitation plan of the project is focused on two possible levels of exploitation: exploitation *within the consortium* and exploitation *outside the consortium*, with an obvious preference for the first option.

Exploitation by the consortium

The first step towards successful exploitation has been made through the formation of the consortium, which was therefore composed in such a way to involve one producer of the final product (Vladipor - SME, membrane and module producer) and one end-user of the final technology (TPI - SME, producer of CO_2 separation plants). Intentionally only one company in each field was chosen to avoid possible internal competition.
Both companies have all the required facilities and - through participation in the consortium - know-how to further develop and commercialize the final products of the research. No teams better than these two SMEs with an excellent knowledge of the precise market needs can evaluate the true potential of the developed technologies. Since they have permanently been informed about the entire process of the new material development, they know exactly the advantages and the limits of every single product, so they can make a realistic evaluation of the true potential. Already in the research phase of membrane development, where Vladipor had an active role, their feedback could lead to a faster achievement of the targets set in the project.
For quantitative evaluation of the potential and exploitability of the project results, an *economic evaluation* of the membrane production at one side and of the entire process at the other side (for CO_2 separation as well as for bioethanol production) was carried out.

The second option to exploit the project results within the consortium by the generation of spin-off companies has not been used because the products have not reached the suitable level of development to become directly exploitable. The knowledge and IPR management plan, as regulated also by the Consortium Agreement, offered in principle the right context and a privileged position to the consortium members to exploit the knowledge generated within the project, also in the form of a spin-off. From the logistic and also economic point of view most partners are supported by their own organizations (e.g. *Liaison Office* of Unical, *Valorization Centre* of TUD, central CNR offices for ITM, Czech government for ICT, Legal and commercial division of CU etc..).

Exploitation outside the consortium

Publicity for the potential exploitation outside the consortium has been made through a thematic workshop for demonstrating the relevance and potential of the newly developed technologies to the scientific as well as the industrial community. In the PUDK, some actions will continue:

- ✓ Industrial partner TPI is involved in a National Operative Programme, in collaboration with ITM, where the final aim is to construct a working separation unit at pilot scale, based on membrane technology. It is not likely that any of the membranes developed and studied within the DoubleNanoMem project will be used in this plant, but the general knowledge generated will be of great use, also when using commercial membranes.
- ✓ Further networking of individual partners of the Consortium.
  - o The TUD team develops the exploitation of biofuel production by fermentation/PV through their numerous contacts and relations with other projects. Companies involved either in fermentative alcohol producers or building up technology in this field, such as Nedalco, Shell, and DuPont, will be approached to exploit the results. The good network of contacts of TUD, in particular with some important companies involved in established research consortia led by **TUD** (*B-basic*, http://www.b-basic.nl/partners.html and the *Kluyver Centre*, http://www.kluyvercentre.nl/content/partners.html will be used to approach potentially interested companies.
  - o Vladipor and TPI, will actively participate in promoting of the knowledge through their extensive network of contacts/clients.

Knowledge and Intellectual property management

Ownership of the project results has been clearly regulated in the consortium agreement. On the basis of the relevant articles, one patent has been filed by the University of Calabria on a novel mixed matrix membrane composition. The final aim of the university is to exploit this patent by selling it to interested parties. The Liaison office of the University is in charge of the actions to be taken.

Another potential patent application, by the Katholieke Universiteit Leuven, was interrupted because of insufficient novelty. The results will now be disseminated through a manuscript, to be published in a high level journal.

During the project, the dissemination of information has always been postponed until verification that non of the beneficiaries had any objections (see section 1.4.3.1). The same procedure to ask authorization for dissemination of foreground will be maintained after the end of the project until

Property Rights and Exploitation

As a rule, knowledge generated within the consortium will be property of the consortium. This does not automatically mean that all partners become the owner of the information generated by a single team or a limited number of teams. However, the aim is that all teams, for the duration of the project, should be able to use this knowledge for the scope of the project under the umbrella of the confidentiality agreement.

In principle, the partner who is responsible for an invention will protect this knowledge by a patent application. In the case of joint inventions, all involved partners will be recognized as the inventors. If one of the teams does not to intend to apply for a patent, the other inventors should have the first option to do this.

In the case of granted patents, based on the results of the project, the other project partners should have the first option for taking a licence on the patent, if the inventor intends to licence the patent. If none of the consortium partners intends to patent an invention then the knowledge may be commercialized to third parties through the exploitation plan.

Background Knowledge management

A similar policy is suggested for background knowledge. Partners are invited to make relevant background knowledge available to other partners in the consortium, under protection of a confidentiality agreement, but they can and must not be obliged to do so.
In principle background IP will remain the property of the existing owner. Subject to pre-existing 3rd party obligations - and for the purposes of undertaking the project - the owner could propose making available any relevant Background IP to consortium members under a royalty-free non-exclusive licence. If access to Background IP is required to enable commercial exploitation of IPR resulting from the project by consortium members, then the owner would propose a licence to its Background IP; the licence to be negotiated on fair and reasonable terms and subject to any pre-existing 3rd party obligations.

1.4.3.3 'Hidden' Exploitation

All academic teams have incremented significantly their knowledge of the MMMs and their constituents. This knowledge will not be lost but will be used as background knowledge in further research. A total of more than 30 research papers, of which 24 already published, several still under evaluation, and three of very high impact (Science, Advanced Materials, Angewandte Chemie) will attract the attention of the scientific as well as industrial community. ITM was contacted for instance by an important Swiss Industry with a specific problem on permselective films where the knowledge on perfluoropolymers could be applied directly in the development of selective films for a M€ application. Tecno Project Industriale is involved in an Italian National Operational Programme for the practical development of a working separation unit for biogas treatment, which will find direct application. Other knowledge will be further cultivated and exploited in basic research projects. CU is further developing its novel polymers in a national project which foresees also scale-up of the polymer synthesis to levels which approach those of commercialization in niche markets.
All teams are thus actively involved in further use and exploitation of their foreground.

1.5 Project public website and relevant contact details

Project website: www.itm.cnr.it/doublenanomem

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10 Tecno Project Industriale s.r.l. (TPI), via Enrico Fermi, 40, 24035 Curno (BG), Italy
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References

1. A.A. Gusev, O. Guseva, *Adv. Mater.*, 19 (2007) 2672.
2. G. Golemme, M. G. Buonomenna, A. Bruno, R. Manes *Eur. Pat* 12170372.2 (2012).
3. A.F. Bushell, P.M. Budd, M.P. Attfield, J.T.A. Jones, T. Hasell, A.I. Cooper, P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen, *Angew. Chem. Int. Ed.*, In Press.
4. A.F. Bushell, M.P. Attfield, C.R. Mason, P.M. Budd, Yu.P. Yampolskii, L. Starannikova, A. Rebrov, F. Bazzarelli, P. Bernardo, J.C. Jansen, M. Lanč, K. Friess, V. Shantarovich, V. Gustov, V. Isaeva, *J. Membr. Sci.*, 427 (2013) 48-62.
5. C.R. Mason, L. Maynard-Atem, N.M. Al-Harbi, P.M. Budd, P. Bernardo, F. Bazzarelli G. Clarizia, J.C. Jansen, *Macromolecules*, 44 (2011) 6471–6479.
6. e.g., O.G. Nik et al., J. Membr. Sci. 379 (2011) 468.
7. K. Friesș, J.C. Jansenņ, F. Bazzarelli, P. Izák, V. Jarmarová, M. Kačírková, J. Schauer, G. Clarizia, P. Bernardo, *J. Membr. Sci*., 415-416 (2012) 801-809.

8 S. Darvishmanesh, F. Tasselli, J.C. Jansen, E. Tocci, F. Bazzarelli, P. Bernardo. P. Luis, J. Degrève, E. Drioli, B. van der Bruggen, *J. Membr. Sci.*, 384 (2011) 89– 96

9 K. Friess, M. Šípek, V. Hynek, P. Sysel, K. Bohatá, P. Izák, *J. Membr. Sci.* 240 (2004) 179.

10 P. Neogi, *AiChE J.* 29 (1983) 829.

11 K. Friess, V. Hynek, M. Šípek, W. M. Kujawski, O. Vopička, M. Zgažar, M. W. Kujawski, *Sep. Purif. Tech.* 80 (2011) 418.

12 K. Friess, J.C. Jansen, O. Vopicka, A. Randová, V. Hynek, M. Šípek, L. Bartovská, P. Izák, M. Dingemans, J. Dewulf, H. Van Langenhove, E. Drioli, *J. Membr. Sci.* 338 (2009) 161.

13 O. Vopička, K. Friess et al., *submitted to J. Membr. Sci.* April 2012

14 J.C. Martins, C. Bailezão, Instituto Superior Tecnico, Lisboa

15 M.G. Buonomenna, et al., *Adv. Funct. Mat.* 22 (2012) 1759.

16 S. Chovau et al., *The Journal of Chemical Thermodynamics* 48 (2012) 260.

17 Woo et al., *Microp. Mesop. Mater.* 110 (2008) 330

18 e.g. D.A. Newsome et al., *Microp. Mesop. Mater.* 107 (2008) 286

19 S. Chovau et al., Bioresource Technology 102 (2011) 1669.

20 S. Gaykawad et al., Bioresource Technology 116 (2012) 9.

21 Kwiatkowski et al., *Ind. Crops Products* 23 (2006) 288.

22 A.F. Bushell, M.P. Attfield, C.R. Mason, P.M. Budd, Yu.P. Yampolskii, L. Starannikova, A. Rebrov, F. Bazzarelli, P. Bernardo, J.C. Jansen, M. Lanč, K. Friess, V. Shantarovich, V. Gustov, V. Isaeva, *J. Membr. Sci.*, 427 (2013) 48-62.

23 A.F. Bushell, P.M. Budd,* M.P. Attfield, J.T.A. Jones, T. Hasell, A.I. Cooper,* P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen*, *Angew. Chem., Int. Edition*, In Press. DOI: 10.1002/anie.201206339

24 C.G. Bezzu, M. Carta, A. Tonkins, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, *Adv. Mater.* 2012, 24, 5930-5933

25 M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown*, *Science*, in press.

2 Use and dissemination of foreground

2.1 A - Dissemination Measures (Public)

The dissemination actions are described extensively in section 1.4.3.1 of this report. The majority of dissemination actions took place through scientific publications (25 accepted, 7 still under evaluation). and through more than 130 oral and poster presentations at national and international conferences and workshops. Some of the work was published in very high impact journals such as *Science*, *Advanced Materials*, *Angewandte Chemie* (Table 2.1). A vast number of journals in different disciplines was used, but as expected the majority of manuscripts was published in the specific Journal of Membrane Science. The average impact factor was 5.45

Table 2.1. Overview of the Manuscripts published or accepted (until December 2012)

	ISI Journal	2011 I.F.	No. articles	Total impact
1	Advanced Materials	13.877	1	13.877
2	Angewandte Chemie, International Edition	13.455	1	13.455
3	Bioresource Technology	4.980	2	9.960
4	Ind. Eng. Chem. Res.	2.237	1	2.237
5	Journal of Chemical Thermodynamics	2.422	1	2.422
6	Journal of Membrane Science	3.850	8	30.800
7	Journal of Physical Chemistry B	3.696	1	3.696
8	Macromolecules	5.167	2	10.334
9	Petroleum Chemistry	0.374	2	0.748
10	Polymer Science Series, A	0.838	1	0.838
11	Science	31.201	1	31.201
12	Separation and Purification Technology	2.921	2	5.842
	Total		**23**	**125.41**
	Average		1.917	5.453
	Non ISI Journal			
1	ACS Symposium Series		1	
2	Book chapter		1	

Some of the work has not been published yet or works is still in progress. There are probably results for at least 5-10 more publications.
In the framework of the DoubleNanoMem project a dedicated workshop was organized on nanostructured and nanocomposite membrane materials, with speakers and poster presenters from inside and outside the consortium. Furthermore, the partners contributed to various other public and professional events.

Some illustrative statistical data on the publications per beneficiary are plotted in Figure 2.1. The left graph shows the total number of manuscript each team is involved in. Both TIPS and ITM have a relatively large number of publications due to their high personnel effort in the project and due to their key role as central test laboratories for the membranes of other teams. The middle graph, these data are normalized for the total number of authors for each team. In these terms, KUL has a remarkably high productivity, given their relatively low number of man months foreseen in the project. In terms of Impact, excluding ITM which is involved in many manuscripts, the impact of CU is highest because their manuscripts were published in very high impact journals only. In total 10 of the manuscripts were co-authored by institutions outside the consortium, which have a high impact in all calculation methods

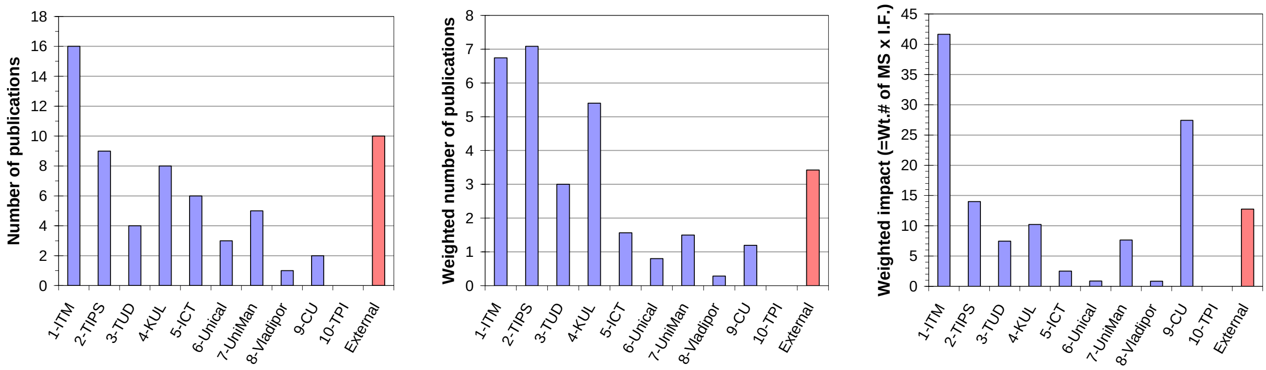

Figure 2.1. Involvement of each beneficiary in the total number of submitted manuscripts. Left: absolute numbers; middle: normalized for the number of authors per team; right: multiplied by the 2011 journal impact factor (accepted papers only).

The collaborative nature of the project is in part reflected in the number of teams involved in each manuscript (Figure 2.2). The majority of manuscripts (15) is written in collaboration with at least one other team, while a few manuscripts involve three or even four different teams. A substantial number of manuscripts (12) is also prepared by a single beneficiary because of the specific topic or because the team possesses all necessary tools for completing the work. The teams of TUD, KUL, Vladipor and CU intensively collaborate internally with no other beneficiaries outside the consortium, while the teams of TIPS and Unical have more external coauthors than internal coauthors. ITM, ICT and UniMan have both internal and external coauthors, with the majority from within the consortium.

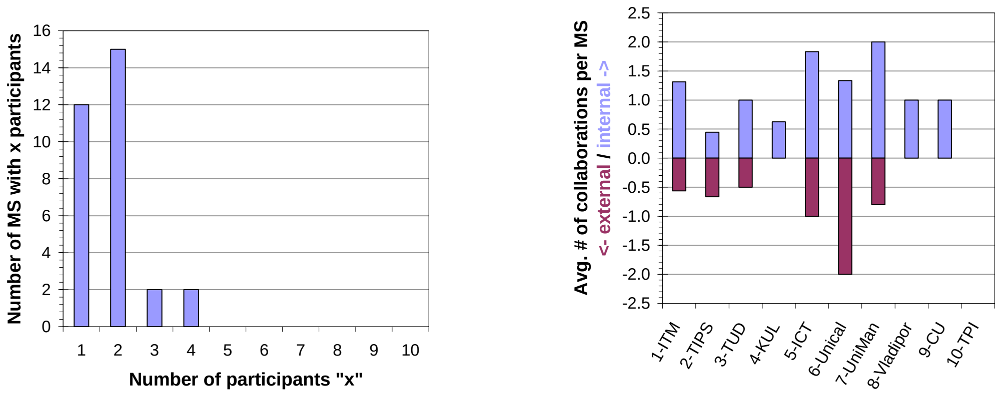

Figure 2.2. Total number of beneficiaries involved in each manuscript, excluding external institutes (left) weighted number of internal collaborations with other beneficiaries and collaborations with external institutes, weighted for the number of authors per team (right).

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES										
No.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publicn.	Year of publicn.	Relevant pages	Permanent identifiers[2] (if available)	Is/Will open access[3] provided to this publication?
1	*An Efficient Polymer-Based Molecular Sieve for Gas Separations*	*M. Carta*	*Science*		*AAAS*	*Washington*	*In press*			
2	*A spirobifluorene-based polymer of intrinsic microporosity with improved performance as a molecular sieve for gas separations*	*C.G. Bezzu*	*Advanced Materials*		*Wiley*	*Weinheim*	*2012*		*DOI: 10.1002/adma.201202393*	*No*
3	*Nanoporous organic polymer/cage composite membranes*	*A.F. Bushell*	*Angewandte Chemie International Edition*		*Wiley Online*	*Weinheim*	*In press*		*DOI: 10.1002/anie.201206339*	*No*
4	*New High Permeable Addition Poly(tricyclononenes) with Si(CH3)3 Side Groups. Synthesis, Gas Permeation Parameters, and Free Volume*	*M. Gringolts*	*Macromolecules*	*No. 43 (17), August 2010*	*American Chemical Society*	*Washington*	*2010*	*pp. 7165–7172*	*DOI: 10.1021/ma100656e*	*No*
5	*Polymer of Intrinsic Microporosity Incorporating Thioamide Functionality: Preparation and Gas Transport Properties*	*C.R. Mason*	*Macromolecules*	*No. 44, July 2011*	*American Chemical Society*	*Washington*	*2011*	*pp. 6471-6479*	*DOI: 10.1021/ma200918h*	*No*
6	*Influence of fermentation by-products on the purification of ethanol from water using pervaporation*	*S. Chovau*	*Bioresource Technology*	*No. 102 (2), January 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 1669-1674*	*DOI: 10.1016/j.biortech.2010.09.092*	*No*
7	*Effects of yeast-originating polymeric compounds on ethanol pervaporation*	*S. Gaykawad*	*Bioresource Technology*	*No. 116, July 2012*	*Elsevier B.V.*	*Amsterdam*	*2012*	*pp. 9-14*	*DOI: 10.1016/j.biortech.2012.04.032*	*No*
8	*Intermolecular Interactions: New Way to Govern Transport Properties of Membrane Materials*	*Y. Yampolskii*	*Industrial & Engineering Chemistry Research*	*No. 49, May 2010*	*American Chemical Society*	*Washington*	*2010*	*pp. 12031-12037*	*DOI: 10.1021/ie100097a*	*No*
9	*Organic vapour transport in glassy*	*J.C. Jansen*	*Journal of Membrane*	*No. 367 (1-2),*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 141-*	*DOI:*	*No*

[2] A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

[3] Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

	perfluoropolymer membranes: A simple semi-quantitative approach to analyze clustering phenomena by time lag measurements		*Science*	*February 2011*				*151*	*10.1016/j.memsci.2010.10.063*	
10	*Solubility controlled permeation of hydrocarbons in novel highly permeable polymers*	*Yu. Grinevich*	*Journal of Membrane Science*	*No. 378 (1-2), August 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 250-256*	*DOI: 10.1016/j.memsci.2011.05.009*	*No*
11	*Novel polyphenylsulfone membrane for potential use in solvent nanofiltration*	*S. Darvishmanesh*	*Journal of Membrane Science*	*No. 379 (1-2), September 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 60-68*	*DOI: 10.1016/j.memsci.2011.05.045*	*No*
12	*Preparation of solvent stable polyphenylsulfone hollow fiber nanofiltration membranes*	*S. Darvishmanesh*	*Journal of Membrane Science*	*No. 384 (1-2), November 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 89-96*	*DOI: 10.1016/j.memsci.2011.09.003*	*No*
13	*Gas transport and free volume in hexafluoropropylene polymers*	*N.A. Belov*	*Journal of Membrane Science*	*No. 383 (1-2), November 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 70-77*	*DOI: 10.1016/j.memsci.2011.08.029*	*No*
14	*Ordering phenomena in nanostructured poly(styrene-b-butadiene-b-styrene) (SBS) membranes for selective ethanol transport*	*M. G. Buonomenna*	*Journal of Membrane Science*	*No. 385-386, December 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 162-170*	*doi: 10.1016/j.memsci.2011.09.035*	*No*
15	*High ionic liquid content polymeric gel membranes: correlation of membrane structure with gas and vapour transport properties*	*K. Friess*	*Journal of Membrane Science*	*No. 415-416, October 2012*	*Elsevier B.V.*	*Amsterdam*	*2012*	*pp. 801-809*	*DOI: 10.1016/j.memsci.2012.05.072*	*No*
16	*Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8, in press*	*A.F. Bushell*	*Journal of Membrane Science*		*Elsevier B.V.*	*Amsterdam*	*2012*		*DOI: 10.1016/j.memsci.2012.09.035*	*No*
17	*Physicochemical Characterization of Transport in Solvent Resistant Nanofiltration: The Effect of Solute Size, Polarity, Charge and Solubility Parameter*	*S. Darvishmanesh,*	*Journal of Physical Chemistry B*	*No. 115, November 2011*	*American Chemical Society*	*Washington*	*2011*	*pp. 14507-14517*	*DOI :10.1021/jp207569m*	*No*
18	*Multilayer composite SBS membranes for pervaporation and gas separation*	*F. Bazzarelli*	*Separation and Purification Technology*	*No. 80/3, August 2011*	*Elsevier B.V.*	*Amsterdam*	*2011*	*pp. 635-642*	*DOI: 10.1016/j.seppur.2011.06.025*	*No*
19	*Gas transport properties of PEBAX®/Room Temperature Ionic Liquid gel membranes*	*P. Bernardo*	*Separation and Purification Technology*	*No. 97, September 2012*	*Elsevier B.V.*	*Amsterdam*	*2012*	*pp. 73-82*	*DOI: 10.1016/j.seppur.2012.02.041*	*No*
20	*Application of the mass-based UNIQUAC model to membrane systems: A critical revision*	*S. Chovau*	*The Journal of Chemical Thermodynamics*	*No. 48, May 2012*	*Elsevier B.V.*	*Amsterdam*	*2012*	*pp. 260-266.*	*DOI: 10.1016/j.jct.2011.12.034*	*No*
21	*Comparison of membrane performance of*	*S. Chovau*	*In: Escobar I., Van*	*No. 1078,*	*American*	*Washington*	*2011*	*pp 51–59*	*DOI: 10.1021/bk-2011-*	*No*

	PDMS-based membranes during ethanol/water pervaporation and fermentation broth pervaporation		der Bruggen B. (Eds.), Modern Applications in Membrane Science and Technology	January 2011	Chemical Society	n			1078.ch005 ISBN13: 9780841226180 eISBN: 9780841226203	
22	Study of the Hyflon AD80 Perfluorinated Copolymer by Inverse Gas Chromatography	N. A. Belov	Polymer Science, Series A	No. 52/8, August 2010	Springer		2010	pp. 781–786	DOI: 10.1134/S0965545X1008002X	No
23	Highly permeable polymer materials based on silicon-substituted norbornenes	M. Gringol'ts	Petroleum Chemistry	No. 50, September 2010	Springer	Heidelberg, Germany	2010	pp. 352-361	DOI: 10.1134/S0965544110050063	No
24	Membrane separation of gaseous C1-C4 alkanes, (Original Russian Text © , published in Membrany i Membrannye Tekhnologii, 2011, Vol. 1, No. 3, pp. 163–173).	Yu. Grinevich	Petroleum Chemistry	No. 51 (8), December 2011	Springer	Heidelberg, Germany	2011	585–594	DOI: 10.1134/S0965544111080044	No
25	Pervaporation	B. Van der Bruggen	'Filtration and Separation Handbook'		Elsevier		to be published in 2014			
Submitted										
26	Critical analysis of techno-economic estimates for the production cost of lignocellulosic bio-ethanol	S. Chovau	Renewable and sustainable energy reviews		Elsevier B.V.	Amsterdam				
27	Novel PIM mixed matrix membranes: the role of silicalite-1on ethanol/water and gas separations	C.R. Mason								
28	Equilibrium and transient sorption of vapors and gases in the polymer of intrinsic microporosity PIM-1	O. Vopicka	Journal of Membrane Science		Elsevier B.V.	Amsterdam				
29	Inverse Gas Chromatography and Thermodynamics of Sorption in Polymers	N. Belov	Vysokomolecuranye soedineniya (Polymer Science)							
30	New nanostructured hybrid membranes: Amine-Functionalized platelet SBA-15 in poly(styrene-b-butadiene-b-styrene) (SBS) matrix leading to enhanced gas separation performance	M.G. Buonomenna	Advanced Materials		Wiley	Weinheim				
31	Pervaporation of ethanol from lignocellulosic fermentation broth	S. Gaykawad	Bioresource Technology		Elsevier B.V.	Amsterdam				

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

No.	Type of activities[4]	Main leader	Title	Date	Place	Type of audience[5]	Size of audience	Countries addressed
1.	*Presentations*	*TIPS*	*Conference for Young Scientists "Macromolecular Nanoobjects and Polymer Nanocomposites"*	*10 November 2009*	*Moscow, Russia*	*Scientific Community (higher education, Research)*	*200*	*Russia, USA, France, Germany*
2.	*Interviews*	*UniCal*	*Web-interview* *G. Golemme*	*22 June 2009*	*UNICAL, Rende (CS), Italy*	*Scientific Community (higher education, Research)*	*1000*	*Italy*
3.	*Press releases*	*ITM*	*Press release on project start*	*30 June 2009*	*ITM-CNR, Rende (CS), Italy*	*Scientific Community (higher education, Research)*	*1000*	*Italy*
4.	*Web sites / Applications*	*ITM*	*Activation of a public project website*	*30 June 2009*	*ITM-CNR, Rende (CS), Italy*	*Scientific Community (higher education, Research)*	*1000*	*All*
5.	*Articles published in the popular press*	*ITM*	*Article on DoubleNanoMem in 'ITM News', the newsletter of ITM-CNR*	*30 June 2009*	*ITM-CNR, Rende (CS), Italy*	*Scientific Community (higher education, Research)*	*1000*	*All*
6.	*Conference, Oral presentation*	*ITM*	*Euromembrane 2009* *J.C. Jansen, et al., Analysis of the free volume distribution in Hyflon® AD glassy perfluoropolymers by photochromic probes: comparison with other techniques*	*6-10 Sept. 2009*	*Montpellier, France*	*Scientific Community (higher education, Research)*	*>500*	*All*
7.	*Conference, Poster presentation*	*ITM*	*Euromembrane 2009* *J.C. Jansen et al. , Transport properties of organic vapours in glassy perfluoropolymer membranes revealed by detailed analysis of the transient behaviour in the permeation curve*	*6-10 Sept. 2009*	*Montpellier, France*	*Scientific Community (higher education, Research)*	*>500*	*All*
8.	*Conference, Oral presentation*	*ICT*	*56th Conference of Chemical and Process Engineering CHISA 2009 (in Czech)* *K. Friess, et al., Comparison of vapour sorption of C1-C4 alcohols and hydrocarbons in amorphous perfluoropolymer*	*19-22 October 2009*	*Srní, Šumava, Czech Republic*	*Scientific Community (higher education, Research)*	*200*	*Czech Republic*
9.	*Conference, Oral presentation*	*UniCal*	*Hybrid Materials* *M.G. Buonomenna et al., SAPO-34/Polyimide, mixed matrix membranes, study of the preparation parameters for optimal, CO2/CH4 separation*	*6-10 March 2011*	*Strasbourg, France*	*Scientific Community (higher education, Research)*	*250*	*All*
10.	*Publication*	*ITM*	*Article on Scienzaonline* *M. A. Liberti, J. C. Jansen, Membrane: una tecnologia pulita*	*20 January*	*ITM-CNR, Rende*	*Scientific community (higher*	*>1000*	*Italy*

[4] A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

[5] A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias ('multiple choices' is possible.

			per un futuro sostenibile	*2010*	*(CS), Italy*	*education, Research) - Industry - Civil society - Policy makers - Medias*		
11.	*Web sites / Applications*	*ITM*	*Activation of the restricted area of the website*	*29 January 2010*	*ITM-CNR, Rende (CS), Italy*		*50*	
12.	*Web sites/Applications*	*UniMan*	*Activation of dedicated website*	*30 January 2010*	*UniMan, Manchester, UK*	*Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias*	*>1000*	*All*
13.	*Web sites/Applications*	*ICT*	*Links on ICT web pages*	*30 January 2010*	*ICT, Prague, Czech Republic*	*Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias*	*>1000*	*all*
14.	*Posters*	*ICT*	*Informative posters about DoubleNanoMem project during MY SCIENCE workshop*	*8 March 2010*	*ICT, Prague, Czech Republic*		200	*all*
15.	*Workshop*	*ICT*	*MY SCIENCE workshop at ICT*	*9 March 2010*	*ICT, Prague, Czech Republic*		200	*all*
16.	*Posters*	*ITM*	*General informative poster during 'ECI Conference 2010'*	*9 May 2010*	*ITM-CNR, Rende (CS), Italy*		200	*all*
17.	*Flyers*	*ITM*	*Informative brochures*	*9 May 2010*	*ITM-CNR, Rende (CS), Italy*	*Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias*	500	
18.	*Conference, Poster presentation*	*TUDelft*	*RRB6 conference* *S.S. Gaykawad et al, Integrated Ethanol fermentation and pervaporation - Basic modeling*	*7-9 June 2010*	*Dusseldorf, Germany*	*Scientific Community (higher education, Research)*	500	All
19.	*Conference, Oral presentation*	*UniCal*	*IZC-IMMS2010, the 16th International Zeolite Conference joint with the 7th International Mesostructured Materials Symposium* *G. Golemme et al., Surface functionalised silicalite-1 (MFI) inside a styrene-butadiene-styrene (SBS) matrix induces ordered phase separation, Oral presentation*	*July 4-10, 2010*	*Sorrento, Italy*	*Scientific Community (higher education, Research)*	250	*All*
20.	*Conference, Poster presentation*	*CU*	*MACRO 2010, 43rd IUPAC World Polymer Congress* *Y. Rogan et al., Polymers of intrinsic microporosity (PIMs) derived from novel 1,1-spirobisindanes*	*11-16 July, 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
21.	*Conference, Poster presentation*	*ITM*	*MACRO 2010* *J. Jansen et al., Transport properties of asymmetric dense PVDF hollow fibre membranes for potential use in gas, vapour and organic liquid separations*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All

22.	*Conference, Oral presentation*	*ICT*	*MACRO 2010* *K. Friess et al., Permeation and sorption properties of PIM-1 Mixed Matrix Membranes filled with tailored nanoparticles*	*11 - 16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
23.	*Conference, Poster presentation*	*ITM*	*MACRO 2010* *E. Tocci et al., Atomistic simulation of a novel polyimide with intrinsic microporosity, PIM-PI*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
24.	*Conference, Poster presentation*	*ITM*	*MACRO 2010* *F. Tasselli et al., Perfluoropolymer-based composite membranes: preparation and gas transport properties*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
25.	*Conference, Oral presentation*	*ITM*	*MACRO 2010* *J.C. Jansen et al., Qualitative and quantitative comparison of different molecular probing techniques for the analysis of the free volume distribution of amorphous glassy perfluoropolymers*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
26.	*Conference, Poster presentation*	*UniCal*	*MACRO 2010* *M.G. Buonomenna et al., Preparation of SAPO-34/Polyimide Mixed Matrix Membranes*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
27.	*Conference, Poster presentation*	*UniMan*	*MACRO 2010* *A. Bushell et al., Composite Membranes of Zeolitic Imidazolate Frameworks (ZIFs) in a Polymer of Intrinsic Microporosity*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
28.	*Conference, Poster presentation*	*UniMan*	*MACRO 2010* *L. Maynard-Atem et al., Alternative synthetic route to PIM-1*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
29.	*Conference, Poster presentation*	*UniMan*	*MACRO 2010* *L. Maynard-Atem et al., The preparation of PIM-1 and its effects on the polymer properties*	*11-16 July 2010*	*Glasgow, UK*	*Scientific Community (higher education, Research)*	500	All
30.	*Conference, Poster presentation*	*UniMan*	*MACRO 2010* *S. Hosna et al., Novel thermally rearrangeable polyimide membrane based on a polymer of intrinsic microporosity (PIM)*	*11-16 July 2010*	*Glasgow, UK.*	*Scientific Community (higher education, Research)*	500	All
31.	*Conference, Poster presentation*	*UniCal*	*NAMS/ICIM 2010* *G. Golemme et al., Performance of Styrene-butadiene-styrene (SBS) membranes for ethanol/water separation (SBS) membranes for ethanol/water separation: pure SBS vs mixed matrix membranes*	*17-22 July 2010*	*Washington D.C., U.S.A.*	*Scientific Community (higher education, Research)*	1000	*All*
32.	*Conference, Poster presentation*	*KUL*	*Gordon Research Conference on Membranes: Materials & Processes* *S. Chovau et al., Bio-ethanol production using a hybrid pervaporation-distillation system: Influence of fermentation by-products on membrane performance*	*25-30 July 2010*	*New London, NH*	*Scientific Community (higher education, Research)*	200	*All*
33.	*Conference, Oral presentation*	*KUL*	*240th National ACS Meeting* *S. Chovau et al., Influence of fermentation by-products on the isolation of ethanol from fermentation broths using pervaporation*	*22-26 August 2010*	*Boston, MA, USA*	*Scientific Community (higher education, Research)*	250	*All*
34.	*Conference,*	*ICT*	*19th International Congress of Chemical and Process*	*28 August - 1*	*Prague, Czech*	*Scientific Community (higher*	250	All

	Oral presentation		Engineering CHISA 2010 K. Friess et al., The effect of cucurbituril-based nanofillers on gas and vapour permeation and sorption properties of styrene-butadiene-styrene polymeric membranes	Sept. 2010	Republic	education, Research)		
35.	Conference, Oral presentation	ICT	19th International Congress of Chemical and Process Engineering CHISA 2010 K. Friess et al., Sorption properties of fluorinated polymers	28 August - 1 Sept. 2010	Prague, Czech Republic	Scientific Community (higher education, Research)	250	All
36.	Conference, Oral presentation	UniCal	10° Convegno Nazionale AIMAT G. Golemme et al., Design, Synthesis and characterization of SAPO-34 crystals for hybrid membranes for the CO2/CH4 separation	5–8 Sept. 2010	Capo Vaticano, Italy	Scientific Community (higher education, Research)	150	Italy
37.	Conference, Oral presentation	TIPS	Russian National Conference MEMBRANY2010 A. Alentiev et al., Novel ways for control of the transport parameters of polymeric membranes	4-8 October 2010	Klyazma, Moscow region, Russia	Scientific Community (higher education, Research)	100	Russia
38.	Exhibitions	TPI	Brau Beviale 2010	10 – 12 November 2010	Nuremberg, Germany	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	1000	All
39.	Conference, Oral presentation	UniCal	International Conference on Composites and Nanocomposites, ICNC 2011 M. G. Buonomenna et al., Functionalised SBA-16 mesoporous oxide: new filler for mixed matrix membranes	7-9 January 2011	Kottayam, Kerala, India	Scientific Community (higher education, Research)	250	All
40.	Exhibitions	TPI	20th Annual Conference of the German Biogas Association with Biogas Trade Fair”	11 January 2011	Nuremberg, Germany	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	1000	All
41.	Conference, Oral presentation	UniCal	241st American Chemical Society National Meeting , “Advances in Process Intensification Symposium” M.G. Buonomenna et al., Novel high free-volume membranes based on poly(bis-SiMe3-tricyclononene) for the pervaporation of ethanol/water mixtures	March 2011	Anaheim, California, USA	Scientific Community (higher education, Research)	500	All
42.	Workshop, Poster presentation	ITM	International Workshop "Characterization of Safe Nanostructured Polymeric Materials" F. Bazzarelli et al., Composite membranes based on Perfluoropolymer: preparation and gas transport	3-4 March 2011	Pozzuoli (NA), Italy	Scientific Community (higher education, Research)	200	All
43.	Workshop, Poster presentation	ITM	International Workshop "Characterization of Safe Nanostructured Polymeric Materials" P. Bernardo et al., Transport properties and physical aging in PIM-1 dense and composite membranes	3-4 March 2011	Pozzuoli (NA) , Italy	Scientific Community (higher education, Research)	200	All
44.	Articles published in	ITM	P. Bernardo, ‘Nanotecnologie contro l'inquinamento	30 March	Italy	Scientific community (higher	1000	Italy

	the popular press		*industriale' in Almanacco della Scienza CNR*	*2011*		*education, Research) - Industry - Civil society - Policy makers - Medias*		
45.	*Conference, Oral presentation*	*TIPS*	*Russian national zeolite conference* *Yu.Yampolskii et al., Composite gas separating membranes containing additives of zeolite ZIF-8*	*June, 2011*		*Scientific Community (higher education, Research)*	*250*	Russia
46.	*Conference, Oral presentation*	*TIPS*	*6th Russian National Zeolite Conference* *Yu.Yampolskii et al., Mixed matrix gas separation membranes containing nano-particles of zeolite-MOF ZIF-8*	*14-16 June 2011*	*Moscow region, Zvenigorod, Russia*	*Scientific Community (higher education, Research)*	*250*	Russia
47.	*Conference, Oral presentation*	*KUL*	*NAMS 2011* *S. Darvishmanesh et al., Novel polyphenylsulfone flat sheet and hollow fiber membranes for organic solvent nanofiltration: preparation and characterisation*	*4-8 June 2011*	*Las Vegas - USA*	*Scientific Community (higher education, Research)*	*500*	All
48.	*Conference, Poster presentation*	*UniCal*	*5th International FEZA Conference* *M.G. Buonomenna et al., SAPO-34 mixed matrix membranes based on PIM-1 and polyimides polymers: role of molecular sieve surface properties and morphology*	*3-7 July 2011*	*Valencia, Spain*	*Scientific Community (higher education, Research)*	*250*	All
49.	*Conference, Oral presentation*	*UniCal*	*5th International FEZA Conference* *M.G. Buonomenna et al., Novel silicalite-1/PIM-1 hybrid nanocomposite membranes for gas separation: preparation and characterization*	*3-7 July 2011*	*Valencia, Spain*	*Scientific Community (higher education, Research)*	*250*	All
50.	*Conference, Oral presentation*	*UniMan*	*MC10 2011 - Tenth International Conference on Materials* *C. Mason et al., Nanocomposite and nanostructured PIM membranes for gas separation*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All
51.	*Conference, Oral presentation*	*UniCal*	*MC10 2011 - Tenth International Conference on Materials* *M.G. Buonomenna et al., Novel mixed matrix membranes based on functionalised SBA-16 mesoporous oxide and a block copolymer of styrene and butadiene (SBS)*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All
52.	*Conference, Oral presentation*	*UniCal*	*MC10 2011 - Tenth International Conference on Materials* *M.G. Buonomenna et al., Effects of synthesis parameters on SAPO-34 morphology and adsorption properties for CO2/CH4 separation*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All
53.	*Conference, Oral presentation*	*UniMan*	*MC10 2011 - Tenth International Conference on Materials* *A. Bushell et al., Composite Membranes of Metal Organic Frameworks (MOFs) in a Polymer of Intrinsic Microporosity*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All
54.	*Conference, Oral presentation*	*ITM*	*MC10 2011 - Tenth International Conference on Materials* *F. Bazzarelli et al., Composite membranes for gas separation applications from highly permeable polymers based on silicon-containing polynorbornene analogs*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All
55.	*Conference, Poster presentation*	*ITM*	*MC10 2011 - Tenth International Conference on Materials* *F. Bazzarelli et al., Composite SBS membranes: coating optimization and scale-up*	*4-11 July 2011*	*Manchester, UK*	*Scientific Community (higher education, Research)*	*400*	All

56.	*Conference, Oral presentation*	*ITM*	*ICOM 2011* *J.C. Jansen et al., Room temperature ionic liquids as carriers for gas and vapour transport in polymer gel membranes*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education, Research)*	*1000*	All
57.	*Conference, keynote*	*UniMan*	*ICOM 2011* *P.M. Budd, Pushing the Bounds: The Quest for Better Membrane Materials*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
58.	*Conference, Poster presentation*	*ICT*	*ICOM 2011* *K. Friess et al., Multicomponent vapour permeation and sorption in high free volume polymers*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
59.	*Conference, Poster presentation*	*ICT*	*ICOM 2011* *K. Friess et al., Gas and vapour permeation and sorption properties of styrene-butadiene-styrene polymeric membranes filled by different macrocyclic nanofillers*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
60.	*Conference, Poster presentation*	*ICT*	*ICOM 2011* *O. Vopicka et al., Equilibrium sorption of vapours of alkanes and alkanols in high free volume polymers*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
61.	*Conference, Poster presentation*	*ICT*	*ICOM 2011* *M. Zgazar et al.,The new models of diffusion coefficient for permeation of organic vapours in polymeric membranes*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
62.	*Conference, Oral presentation*	*TIPS*	*ICOM 2011* *Y. Yampolskii et al., Mixed matrix gas separation membranes based on PIM-1 and nano-particles of zeolite-MOF ZIF-8*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
63.	*Conference, Oral presentation*	*TIPS*	*ICOM 2011* *Y. Yampolskii et al., Solubility controlled separation of hydrocarbons C1-C4 using novel high free volume polymeric membranes*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
64.	*Conference, Poster presentation*	*ITM*	*ICOM 2011* *F. Tasselli et al., Composite membranes based on highly permeable poly(3,4-TCNSi2) for gas separation applications*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
65.	*Conference, Poster presentation*	*ITM*	*ICOM 2011* *P. Bernardo et al., SBS composite membranes: from laboratory scale preparation to module production*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
66.	*Conference, Poster presentation*	*ITM*	*ICOM 2011* *F. Bazzarelli et al., Transport properties and physical aging phenomena in neat and composite PIM-1 membranes for gas and vapour separation applications*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
67.	*Conference, Poster presentation*	*KUL*	*ICOM 2011* *S. Darvishmanesh et al., Preparation and characterization of self-made novel polyphenylsulfone flat sheet and hollow fiber membranes for organic solvent nanofiltration*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
68.	*Conference, Poster presentation*	*UniMan*	*ICOM 2011* *C.R. Mason et al., Nanocomposite PIM membranes for gas*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All

			separation					
69.	*Conference, Poster presentation*	*UniCal*	*ICOM 2011* *M.G. Buonomenna et al., Functionalised SBA-16 mesoporous oxides: new filler for mixed matrix membranes*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
70.	*Conference, Poster presentation*	*UniCal*	*ICOM 2011* *M. G. Buonomenna et al., Novel mixed-matrix membranes composed of silicalite-1 crystals in a poly(styrene-b-butadiene-b-styrene) matrix*	*23-29 July 2011*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*1000*	All
71.	*Conference,*	*ICT*	*ACS meeting* *K. Friess et al., Gas and Vapor Sorption in High Free Volume Polymers (abstract submitted, but not participated)*	*Aug. 28 - Sept. 1, 2011*	*Colorado, USA*	*Scientific Community (higher education*	*0*	All
72.	*Conference, oral presentation*	*ITM*	*ILSEPT 2011, 1st International Conference on Ionic Liquids in Separation and Purification Technology* *J.C. Jansen et al., Modulation of gas transport properties of PEBAX membranes by Room Temperature Ionic Liquids*	*4–7 Sept. 2011*	*Sitges, Spain*	*Scientific Community (higher education*	*300*	All
73.	*Conference, oral presentation*	*ITM*	*ILSEPT 2011* *J.C. Jansen et al., Fluoropolymer/Room Temperature Ionic Liquid gels as membranes for gas and vapour separations*	*4–7 Sept. 2011*	*Sitges, Spain*	*Scientific Community (higher education*	*300*	All
74.	*Conference, Oral presentation*	*ITM*	*XX Convegno Italiano di Scienza e Tecnologia delle Macromolecole* *F. Bazzarelli et al., Composite membranes based on high free volume polymers: preparation and performance*	*4–8 Sept. 2011*	*Terni, Italy*	*Scientific Community (higher education, Research)*	*200*	Italy
75.	*Conference, Oral presentation*	*UniMan*	*ACS Fall meeting 2011, "Chemistry of Air, Space, and Water", ACS, Division of Polymeric Materials: Science and Engineering* *P.M. Budd et al., Nanocomposite gas separation membranes with polymer of intrinsic microporosity (PIM) matrix*	*28 August – 1 Sept. 2011*	*Denver, Colorado, USA*	*Scientific Community (higher education, Research)*	*400*	All
76.	*Conference, Oral presentation*	*TIPS*	*Russian National School on "Macromolecular nano-objects and polymeric nanocomposites"* *Yu. Yampolskii et al., Hybrid nanocomposites: a novel type of membrane materials*	*23-28 October 2011*	*Moscow region , Russia*		*100*	Russia
77.	*Conference, Oral presentation*	*TUDelft*	*1st European Congress of Applied Biotechnology* *S.S. Gaykawad et al., Continuous staged ethanol fermentation coupled with pervaporation*	*25 - 29 Sept. 2011*	*Berlin, Germany*	*Scientific Community (higher education, Research)*	*1000*	All
78.	*Conference, Oral presentation*	*TUDelft*	*11th Netherlands Process Technology Symposium (NPS11)* *S.S. Gaykawad et al., Effects of cellular polymers on membrane performance in pervaporation integrated with fermentation*	*24 -26 October 2011*	*Papendal Arnhem, The Netherlands*	*Scientific Community (higher education, Research)*	*600*	*The Netherlands*
79.	*Conference, Oral presentation*	*KUL*	*International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation* *S. Chovau et al., Improved Description of Sorption Equilibrium*	*8-11 Sept. 2011*	*Torun, Poland*	*Scientific Community (higher education, Research)*	*200*	All

			in Pervaporation by the UNIQUAC Model					
80.	*Conference, Oral presentation*	*KUL*	*11th International Chemical and Biological Engineering Conference, CHEMPOR 2011* *S. Chovau et al., Comparison of membrane performance of PDMS-based membranes during ethanol/water pervaporation and fermentation broth pervaporation*	*5-7 Sept. 2011*	*Caparica (Lisbon), Portugal*	*Scientific Community (higher education, Research)*	*250*	All
81.	*Seminar*	*UniCal*	*Topchiev Institute of Petrochemical Synthesis* *G. Golemme, M.G. Buonomenna, Nanostructured and mixed matrix membranes for molecular separations*	*20 January 2012*	*Moscow, Russia*	*Scientific Community (higher education*	*50*	Russia
82.	*Seminar*	*UniCal*	*Topchiev Institute of Petrochemical Synthesis* *G. Golemme, M.G. Buonomenna, Nanostructured and mixed matrix membranes for molecular separations*	*19 January 2012*	*Moscow, Russia*	*Scientific Community (higher education*	*50*	Russia
83.	*Conference, Oral presentation*	*UniCal*	*EPS International Engineering Forum* *M.G. Buonomenna et al., Membrane operations for the energy and the petrochemical industry*	*24-27 April 2012*	*Montréal, Canada*	*Scientific Community (higher education, Research)*	*500*	All
84.	*Conference, Oral presentation*	*TUDelft*	*RRB-8* *S.S. Gaykawad, Integration of ethanol fermentation and pervaporation*	*6th June 2012*	*Toulouse, France*	*Scientific Community (higher education, Research)*	*600*	All
85.	*Conference, Poster presentation*	*UniCal*	*ICIM12 Conference* *G. Golemme et al., Resistance to transport of H2 through the external surface of as-made and modified silicalite-1*	*9-13 July 2012*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*400*	All
86.	*Conference, Poster presentation*	*UniCal*	*ICIM12 Conference* *M.G. Buonomenna et al., SBS/SBA-15 mixed matrix membranes for the effective removal of nitrogen from natural gas*	*9-13 July 2012*	*Amsterdam, The Netherlands*	*Scientific Community (higher education*	*400*	All
87.	*Conference, Oral presentation*	*UniMan*	*World Polymer Congress (MACRO2012)* *P.M. Budd et al., Mixed matrix membranes with a polymer of intrinsic microporosity*	*24-29 June 2012*	*Virginia Tech, USA*	*Scientific Community (higher education*	*800*	All
88.	*Conference, Oral presentation*	*Unical*	*International Symposium on Zeolites and MicroporousCrystals 2012 (ZMPC2012)* *G. Golemme et al., Resistance to transport of H2 through the external surface of as-made and modified silicalite-1*	*July 28 – Aug. 1, 2012*	*Hiroshima, Japan*	*Scientific Community (higher education, Research)*	*400*	*All*
89.	*Workshop, keynote presentation*	*KUL*	*DoubleNanoMem Workshop "Nanostructured And Nanocomposite Membranes For Gas And Vapour Separations"* *B. van der Bruggen, S. Chovau, Prospects on the use of pervaporation for purification of bio-ethanol*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
90.	*Workshop, oral presentation*	*TUDelft*	*DoubleNanoMem Workshop* *A.J.J. Straathof, S.S. Gaykawad, Integration of ethanol fermentation and pervaporation*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
91.	*Workshop, Keynote presentation*	*UniMan*	*DoubleNanoMem Workshop* *P.M. Budd, et al., Nanocomposite membranes with PIM-1*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All

			matrix					
92.	Workshop, oral presentation	CU	DoubleNanoMem Workshop N.B. McKeown et al., Synthesis and properties of Polymers of Intrinsic Microporosity (PIMs)	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
93.	Workshop, oral presentation	ITM	DoubleNanoMem Workshop E. Menna et al., Synthesis of carbon nanotube derivatives as nanofillers	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
94.	Workshop, oral presentation	UniCal	DoubleNanoMem Workshop J. B.Nagy et al., Helical Carbon Nanotubes and Nanocomposites: Mechanical and Flame-retardant Properties and Perspectives in Separation Membranes	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
95.	Workshop, oral presentation	TIPS	DoubleNanoMem Workshop Y. Yampolskii, Lessons learnt in DoubleNanoMem: road map, pits and bumps in mixed matrix membranes	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
96.	Workshop, oral presentation	ICT	DoubleNanoMem Workshop K. Friess et al., Study of transport of gases and vapours in high free volume polymers	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
97.	Workshop, oral presentation	UniCal	DoubleNanoMem Workshop M.G. Buonomenna, G. Golemme, Mixed matrix membranes containing molecular sieves and mesoporous silicas	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
98.	Workshop, oral presentation	ITM	DoubleNanoMem Workshop J. C. Jansen et al., Modulation of the gas and vapour transport in polymeric membranes by ionic liquids	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
99.	Workshop, Poster presentation	ITM	DoubleNanoMem Workshop E. Fabris, et al., Synthesis and characterization of MWNT derivatives as fillers for membrane polymers	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
100.	Workshop, Poster presentation	ITM	DoubleNanoMem Workshop E. Tocci et al., Intrinsic Microporosity polymers(TB-PIMs) membrane of new generation: A Molecular dynamics study of gas transport properties and free volume distribution	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
101.	Workshop, Poster presentation	UniCal	DoubleNanoMem Workshop M. Macchione, et al., Composite membranes for gas separation containing aligned multiwalled carbon nanotubes	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
102.	Workshop, Poster presentation	UniCal	DoubleNanoMem Workshop E. Maccallini, et al., Barrier for the transport of H2 on the surface of silicalite-1 (MFI)	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
103.	Workshop, Poster presentation	UniCal	DoubleNanoMem Workshop A. Santaniello, et al., Phenomenological modeling of mixed matrix membranes containing molecular sieves for gas separations	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
104.	Workshop, Poster presentation	UniCal	DoubleNanoMem Workshop M.G. Buonomenna, et al., SAPO-34 for mixed matrix	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All

			membranes: synthesis and characterization					
105.	*Workshop, Poster presentation*	*UniCal*	*DoubleNanoMem Workshop* *M.G. Buonomenna et al., Organophilic SBS/silicalite-1 mixed matrix membranes*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
106.	*Workshop, Poster presentation*	*UniCal*	*DoubleNanoMem Workshop* *M.G. Buonomenna et al., SBS/Mesoporous silica membranes for gas separation*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
107.	*Workshop, Poster presentation*	*UniMan*	*DoubleNanoMem Workshop* *C.R. Mason et al., Postmodification of PIM-1 and the effect on Gas Transport Properties*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
108.	*Workshop, Poster presentation*	*UniMan*	*DoubleNanoMem Workshop* *B. Satilmis et al., Controlling the surface chemistry of PIMs*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
109.	*Workshop, Poster presentation*	*CU*	*DoubleNanoMem Workshop* *R. Malpass-Evans et al., New Polymers of Intrinsic Microporosity prepared using Tröger's base formation (TB-PIMs)*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
110.	*Workshop, Poster presentation*	*CU*	*DoubleNanoMem Workshop* *M. Lee et al., New Polyimides of Intrinsic Microporosity (PIM-PI)*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
111.	*Workshop, Poster presentation*	*CU*	*DoubleNanoMem Workshop* *M. Carta et al., Synthesis and properties of hexaphenylbenzene-based Polymers of Intrinsic Microporosity (HPB-PIMs)*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
112.	*Workshop, Poster presentation*	*CU*	*DoubleNanoMem Workshop* *C. G. Bezzu et al., Synthesis and properties of a spirobisfluorene-based Polymer of Intrinsic Microporosity (SBF-PIM)*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
113.	*Workshop, Poster presentation*	*ICT*	*DoubleNanoMem Workshop* *M. Lanč et al., Gas sorption in polymers with intrinsic microporosity*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
114.	*Workshop, Poster presentation*	*ICT*	*DoubleNanoMem Workshop* *K. Pilnáček et al., Transport parameters of single species and their mixtures in nanostructured polymers*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
115.	*Workshop, Poster presentation*	*ITM*	*DoubleNanoMem Workshop* *A. Figoli et al., Ethanol removal from water by Pervaporation using SBS membranes in both flat and spiral wound module configuration*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
116.	*Workshop, Poster presentation*	*ITM*	*DoubleNanoMem Workshop* *F. Bisignano et al., Carbon dioxide adsorption on the outer wall of functionalized CNTs with CO2-philic chemical groups: a computational investigation*	*15-18 May 2012*	*Cetraro (CS), Italy*	*Scientific Community (higher education*	*80*	All
117.	*Workshop,*	*ITM*	*DoubleNanoMem Workshop*	*15-18 May*	*Cetraro (CS), Italy*	*Scientific Community (higher*	*80*	All

	Poster presentation		P. Bernardo et al., Effect of post-treatment and physical aging on the gas transport properties of PIM-1 membranes	2012		education		
118.	Workshop, Poster presentation	ITM	DoubleNanoMem Workshop F. Bazzarelli et al., Composite membranes based on high free volume polymers for gas separation	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
119.	Workshop, Poster presentation	ITM	DoubleNanoMem Workshop V. Jarmarová et al., Separation of volatile organic compounds from air by PEBAX®/room temperature ionic liquid gel membranes	15-18 May 2012	Cetraro (CS), Italy	Scientific Community (higher education	80	All
120.	Conference, Oral presentation	Unical	EPS International Chemical Engineering Forum M. G. Buonomenna et al., Membrane operations for the energy and the petrochemical industry	26-27 April 2012	Montreal, Canada	Scientific Community (higher education, Research)	400	All
121.	Conference, Oral presentation	ICT	20th International Congress of Chemical and Process Engineering – CHISA2012 K. Friess et al., Mixed matrix membranes based on styrene-butadiene-styrene with various nanofillers for gas and vapour separations	25-29 August 2012	Prague, Czech Republic	Scientific Community (higher education	250	All
122.	Conference, Keynote presentation	UniMan	CHISA2012 P. Budd, Nanocomposite membrane materials for gas and vapour separations	25-29 August 2012	Prague, Czech Republic	Scientific Community (higher education	250	All
123.	Conference, Oral presentation	ITM	CHISA2012 J.C. Jansen et al., Polymer based ionic liquid gel membranes for gas and vapour separations	25-29 August 2012	Prague, Czech Republic	Scientific Community (higher education	250	All
124.	Conference, Poster presentation	ITM	CHISA2012 P. Bernardo et al., Effect of post-treatment and physical aging on the gas transport properties of PIM-1 membranes	25-29 August 2012	Prague, Czech Republic	Scientific Community (higher education	250	All
125.	Conference, Oral presentation	ICT	CHISA2012 K. Pilnácek et al., Binary vapour mixture permeation through the polymer of intrinsic microporosity PIM-1	25-29 August 2012	Prague, Czech Republic	Scientific Community (higher education	250	All
126.	Internal seminars, oral presentation	ITM	ITM Seminar days P. Bernardo et al., Development of nanostructured and nanocomposite polymer membranes for gas and vapour separations	11-12 Sept. 2012	Rende, Italy	Scientific Community (higher education	50	Italy
127.	Internal seminars, oral presentation	ITM	ITM Seminar days E. Tocci et al., Molecular modelling and permeation properties in polymers of intrinsic microporosity (PIMs)	11-12 Sept. 2012	Rende, Italy	Scientific Community (higher education	50	Italy
128.	Internal seminars, poster presentation	ITM	ITM Seminar days F. Bazzarelli et al., New Composite Membranes based on High Free Volume Polymers: Perspectives and Limits in Gas Separations	11-12 Sept. 2012	Rende, Italy	Scientific Community (higher education	50	Italy
129.	Invited lecture	ITM	Institute of Chemical Technology Prague Seminars	19 Sept. 2012	Prague, Czech Republic	Scientific Community (higher education	50	Czech Republic

			J.C. Jansen, Gas and vapour transport in polymeric membrane systems: Polymers with Intrinsic Microporosity and Ionic Liquid Polymer Gels					
130.	*Conference, poster presentation*	*ITM*	*Euromembrane 2012* *P. Bernardo et al., Physical Aging Study of Post-treated PIM-1 Membranes: Effect on Gas Transport Properties*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
131.	*Conference, poster presentation*	*ICT*	*Euromembrane 2012* *M. Minelli et al., Non Equilibrium modeling of sorption of gases and vapors in Polymers of Intrinsic Microporosity (PIM)*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
132.	*Conference, Poster presentation*	*ICT*	*Euromembrane 2012* *K. Friess et al., Multicomponent gas and vapour sorption in high free volume polymers*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
133.	*Conference, oral presentation*	*ITM*	*Euromembrane 2012* *J.C. Jansen et al., Analysis of gas and vapour transport in novel polymers of intrinsic microporosity (PIMs)*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
134.	*Conference, oral presentation*	*ITM*	*Euromembrane 2012* *J.C. Jansen et al., Characterization of the gas transport in mixed matrix membranes based on polymers with intrinsic microporosity (PIMs)*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
135.	*Conference, poster presentation*	*ITM*	*Euromembrane 2012* *V. Jarmarová et al., Separation of volatile organic compounds from air by PEBAX®/room temperature ionic liquid gel membranes*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
136.	*Conference, poster presentation*	*ICT*	*Euromembrane 2012* *K. Pilnáček et al., Determination of mixed gas permeability of high free volume polymers using direct mass spectrometric analysis of the gas compositions*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
137.	*Conference, poster presentation*	*ITM*	*Euromembrane 2012* *F. Tasselli et al., PEBAX®-based Composite Hollow Fibre Membranes for Gas Separation*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All
138.	*Conference, oral presentation*	*ITM*	*Euromembrane 2012* *E. Tocci et al., Intrinsic Microporosity polymers (TB-PIMs) membrane of new generation: molecular modelling and permeation properties*	*23-27 Sept. 2012*	*London, UK*	*Scientific Community (higher education*	*700*	All

2.2 Section B (Confidential[6] or public: confidential information to be marked clearly)

2.2.1 Part B1

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights[7]:	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
Patent	Yes	30/11/2013	EP12170372.2, 2012	Method for preparing hydrophobic fluorinated mixed matrix membranes, said membranes, and separation methods using said membranes	Università della Calabria G. Golemme, M. G. Buonomenna, A. Bruno, R. Manes

[6] Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

[7] A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

2.2.2 Part B2

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
1. General Advancement of Knowledge	This class of high permeability polymers strongly extends the chemistry of novel membrane materials	No	---	New Poly(norbornene) high FV polymers, fully characterised	C20.1.6 Manufacture of plastics in primary forms M72 Scientific Research and Development	2010	Scientific dissemination (Background already patented)	TIPS *(owner)*
2. Commercial exploitation of R&D results	New polymers are being prepared, which may have better performance as membrane-forming materials than existing polymers.	No	---	Novel PIMs and PIM-PIs and block copolymers, fully characterised	C20.1.6 Manufacture of plastics in primary forms M72 Scientific Research and Development	2011 +	Scientific publications (Background already patented)	UniMan (Owner) CU *(Owner)*
3. Commercial exploitation of R&D results	Molecular sieves and mesoporous materials with functional groups for the controlled transport of gases and vapours have not been commercialized so far	yes	30/11/2013	Novel inorganic nanofillers (zeolites and mesoporous materials) with controlled structure and geometry and functional groups	C23 Manufacture of other non-metallic mineral products M72 Scientific Research and Development	2015	EP12170372.2, 2012 (patent on MMMs)	Unical *(owner)*
4. Commercial exploitation of R&D results	Nanotubes with functional groups for the controlled transport of gases and vapours have not been commercialized so far	yes	01/01/2016	New CNTs with controlled structure and geometry and functional groups	C20.5 Manufacture of other chemical products M72 Scientific Research and Development	2012 2013	Presentation unpatentable results Patents	Unical *(owner)*, ITM-Padua

[8] A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.
[9] A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
5. General advancement of knowledge	Synthesis of novel macrocyclic compounds and their successful modification in order to suppress polymer-filler phase separation	No	---	Modified cucurbituril derivatives, fully characterized	C20.5 Manufacture of other chemical products M72 Scientific Research and Development	2012	Presentations of scientific achievements	ICT *(owner)*
6. General Advancement of Knowledge	The best representatives of a new class of high permeability, high free volume, saturated membrane materials; allows removal of higher hydrocarbons from methane	No	---	Novel Poly(tricyclononenes) containingSiMe3 groups, fully characterized	C20.1.6 Manufacture of plastics in primary forms M72 Scientific Research and Development	2010	Scientific publication (Background already patented)	TIPS *(owner)*
7. Commercial exploitation of R&D results	The combination of highly permeable PFP membranes and porous filler particles has not been explored so far and improves both permeability and selectivity in the CO2/CH4 separation up to the Robeson upper bound.	yes	30/11/2013	Novel hybrid membranes with glassy perfluoropolymer matrix, fully characterised	C22.2.9 Manufacture of other plastic products M72 Scientific Research and Development	2015 2011	EP12170372.2, 2012 (patent by Unical on MMMs) Dissemination of non-patentable results	Unical (Owner), ITM, Vladipor, TIPS
8. General advancement of knowledge	PIM membranes containing new fillers, including MOFs, with improved permselectivity for gas separation	No	---	Novel hybrid membranes with PIM and PIM-PI matrix, fully characterised	C22.2.9 Manufacture of other plastic products M72 Scientific Research and Development	2011	Dissemination of non-patentable results	UniMan (owner), Unical (owner), CU, ITM, TIPS, ICT
9. General advancement of knowledge	Novel SBS-based MMMs, which yield improved performances in organophilic pervaporation (ethanol/water) and possibly in gas separation with respect to SBS.	No	---	Novel hybrid membranes with rubbery (PDMS, SBS) matrix, fully characterised	C22.2.9 Manufacture of other plastic products M72 Scientific Research and Development	2011 +	Presentation of non-patentable results	Unical (owner), ITM (owner), ICT, TIPS

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
10. General advancement of knowledge	Few examples of the orientation of filler particles of MMMs have been reported. The combination with highly permeable polymers is unique.	No	---	Design criteria for mixed matrix membranes with oriented nanofiller particles	M72 Scientific Research and Development C22.2.9 Manufacture of other plastic products	2012	Presentation of alignment approaches of CNTs	Unical (owner), ITM
11. Commercial exploitation of R&D results	Integrated solution for advanced separation comprising improved separation with novel membranes. The specific combination of nanofillers and high free volume polymers is new for this application. Traditional membranes are mostly based on PDMS or analogous polymers and related MMMs	Yes	01/01/2016	Membrane module for pervaporation based on the novel materials, fully characterised	C22.2.9 Manufacture of other plastic products	2012 2015	Internal use. No protection, direct sales by Vladipor without disclosure of materials	Vladipor *(owner),* TU Delft, KU Leuven, ITM, UniMan, TIPS, Unical
12. Commercial exploitation of R&D results	The specific combination of nanofillers and high free volume polymers is new for this application and exceed in performance most, traditional membranes, usually based on simple glassy polymers. Also composite modules with e.g. supported PNB or PIM are novel	Yes	01/01/2016	Membrane module for CO2 separation, fully characterised	C22.2.9 Manufacture of other plastic products	2012 2015	Internal use. No protection, direct sales by Vladipor without disclosure of materials	Vladipor (Owner) , TPI, UniMan, TIPS, ITM

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
13. Commercial exploitation of R&D results	Pilot plant for CO2 capture from flue gas/biogas streams using high efficiency composite membrane modules developed in this project and/or commercial membranes.	Yes	17/05/2012	Working practical gas separation unit, preferably based on an experimental module	C20.1.1 Manufacture of industrial gases	2011 2012	Internal use for the project progress Presentation at DoubleNanoMem workshop	TPI (owner), ITM, Vladipor
14. General advancement of knowledge	The practical application of the novel polymers requires their availability at sufficiently large scale. Optimized procedures will be found for scale-up of laboratory experiments.	No	---	Optimised protocol for the preparation of the innovative polymers	M72 Scientific Research and Development C20.1.6 Manufacture of plastics in primary forms	2012	No. Internal use without disclosing	TIPS, UniMan, CU (owners)
15. General advancement of knowledge	Scale-up of nanofiller synthesis requires highly optimized synthetic procedures with reduced starting materials consumption or reduced reaction and purification times. Scale-up procedures concern those fillers found most suitable at lab-scale.	No	---	Protocol for the production of nanofiller batches of at least 10 g	M72 Scientific Research and Development C20.5 Manufacture of other chemical products	2012	No. Internal use without disclosing	Unical, UniMan (owners), ICT, ITM-Padua
16. Commercial exploitation of R&D results	Innovative method and protocol for binding functional groups on the CNT/inorganic fillers with specific affinity towards the polymer matrix. Also other approaches to improve compatibility with the organic polymers, such as the use of fully organic or metal-organic fillers.	Yes	30/11/2013 (patent)	Protocol for the compatibilization of CNT and inorganic nanofiller particles with the polymer matrix or alternative approaches (use of MOFs or fully organic fillers).	M72 Scientific Research and Development C20.5 Manufacture of other chemical products	2015 2011	EP12170372.2, 2012 (patent by Unical on MMMs) Dissemination of non-patentable results	Unical, UniMan, ITM-Padua, TIPS (Owners) Vladipor, ITM

Type of Exploitable Foreground[8]	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[9]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
17. General advancement of knowledge	Casting of selective layers of composite membranes is done for instance by applying colloid mixtures on a microporous support or on a support containing a highly permeable intermediate layer. Such method allows to produce thin defect-free selective layers from various polymers, including fragile (PIM) or containing various additives (AF 2400+MFI).	Yes	01/01/2016	Coating technique for the preparation of composite membranes of nanostructured membrane materials on a suitable flat sheet or Hollow Fibre support	C22.2.9 Manufacture of other plastic products	2011	Internal use only without disclosure of procedures	Vladipor, ITM (owner), Unical, UniMan, TIPS, CU
18. General advancement of knowledge	Model describing for the novel membranes the input-output relation between individual components' properties and MMM performance Models for correlation of polymer structure and transport	No	---	Macroscopic models of MMMs' performance. Molecular models of polymer structure	M72 Scientific Research and Development	2012 2013	Publications and presentations on MMMs Publication on molecular model	*KU Leuven, Unical (owners)* *ITM (owner)*
19. General advancement of knowledge	Novel concept of NF membranes preparation based on the use of polymer blends	No	---	Novel nanofiltration membranes	C22.2.9 Manufacture of other plastic products	2013	Publication of Results (Materials patent was planned for 2012 but application not filed for insufficient novelty)	*KU Leuven (owner) ITM*

3 Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A	**General Information** *(completed automatically when **Grant Agreement number** is entered.*
Grant Agreement Number:	228631
Title of Project:	DoubleNanoMem
Name and Title of Coordinator:	Dr. ir. Johannes Carolus Jansen

B Ethics	
1. Did your project undergo an Ethics Review (and/or Screening)? • If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports? Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 'Work Progress and Achievements'	***0Yes • No***
2. Please indicate whether your project involved any of the following issues (tick box) :	***YES***
RESEARCH ON HUMANS	
• Did the project involve children?	No
• Did the project involve patients?	No
• Did the project involve persons not able to give consent?	No
• Did the project involve adult healthy volunteers?	No
• Did the project involve Human genetic material?	No
• Did the project involve Human biological samples?	No
• Did the project involve Human data collection?	No
RESEARCH ON HUMAN EMBRYO/FOETUS	
• Did the project involve Human Embryos?	No
• Did the project involve Human Foetal Tissue / Cells?	No
• Did the project involve Human Embryonic Stem Cells (hESCs)?	No
• Did the project on human Embryonic Stem Cells involve cells in culture?	No
• Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	No
PRIVACY	
• Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	No
• Did the project involve tracking the location or observation of people?	No
RESEARCH ON ANIMALS	
• Did the project involve research on animals?	No
• Were those animals transgenic small laboratory animals?	No

• Were those animals transgenic farm animals?	No
• Were those animals cloned farm animals?	No
• Were those animals non-human primates?	No
RESEARCH INVOLVING DEVELOPING COUNTRIES	
• Did the project involve the use of local resources (genetic, animal, plant etc)?	No
• Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	No
DUAL USE	
• Research having direct military use	No
• Research having the potential for terrorist abuse	No

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	**1**	**1**
Work package leaders	**2**	**8**
Experienced researchers (i.e. PhD holders)	**15**	**31**
PhD Students	**6**	**10**
Other	**22**	**28**

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	**19**
Of which, indicate the number of men: 9	**10**

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project?

○ Yes
● No

6. Which of the following actions did you carry out and how effective were they?

	Not at all effective … Very effective
❑ Design and implement an equal opportunity policy	○ ○ ○ ○ ○
❑ Set targets to achieve a gender balance in the workforce	○ ○ ○ ○ ○
❑ Organise conferences and workshops on gender	○ ○ ○ ○ ○
❑ Actions to improve work-life balance	○ ○ ○ ○ ○
● Other:	Existing institutional guidelines followed, without new policy

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

○ Yes- please specify

● No

E	**Synergies with Science Education**	
8.	**Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?**	
	○ Yes- please specify	
	● No	
9.	**Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?**	
	○ Yes- please specify	
	● No	

F	**Interdisciplinarity**		
10.	**Which disciplines (see list below) are involved in your project?**		
	● Main discipline[10]: **1.3 Chemical Sciences**		
	● Associated discipline[10]: **2.3 Other engineering sciences**	○	Associated discipline[10]:

[10] Insert number from list below (Frascati Manual).

G	Engaging with Civil society and policy makers		
11a	**Did your project engage with societal actors beyond the research community?** *(if 'No', go to Question 14)*	○ ●	Yes No

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

- ● No
- ○ Yes- in determining what research should be performed
- ○ Yes - in implementing the research
- ○ Yes, in communicating /disseminating / using the results of the project

11c	**In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?**	○ ●	Yes No

12. Did you engage with government / public bodies or policy makers (including international organisations)

- ● No
- ○ Yes- in framing the research agenda
- ○ Yes - in implementing the research agenda
- ○ Yes, in communicating /disseminating / using the results of the project

13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?

- ○ Yes – as a **primary** objective (please indicate areas below- multiple answers possible)
- ● Yes – as a **secondary** objective (please indicate areas below - multiple answer possible)
- ○ No

13b If Yes, in which fields?

Agriculture Audiovisual and Media Budget Competition Consumers Culture Customs Development Economic and Monetary Affairs Education, Training, Youth Employment and Social Affairs	● Energy Enlargement Enterprise ● Environment External Relations External Trade Fisheries and Maritime Affairs Food Safety Foreign and Security Policy Fraud Humanitarian aid	Human rights Information Society Institutional affairs Internal Market Justice, freedom and security Public Health Regional Policy ● Research and Innovation Space Taxation Transport

13c If Yes, at which level?

- ○ Local / regional levels
- ○ National level
- ○ European level
- ● International level

H Use and dissemination

14. How many Articles were published/accepted for publication in peer-reviewed journals?	**25 (Dec. 2012)**
To how many of these is open access[11] provided?	**0**
How many of these are published in open access journals?	**0**
How many of these are published in open repositories?	**0**
To how many of these is open access not provided?	**all**
Please check all applicable reasons for not providing open access:	
☒ publisher's licensing agreement would not permit publishing in a repository ☐ no suitable repository available ☐ no suitable open access journal available ☐ no funds available to publish in an open access journal ☐ lack of time and resources ☒ lack of information on open access ☒ other[12]:**No existing institutional policies yet** ……………	

15. How many new patent applications ('priority filings') have been made? *("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).*		**1**
16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	Trademark	**0**
	Registered design	**0**
	Other	**0**
17. How many spin-off companies were created / are planned as a direct result of the project?		**0**
Indicate the approximate number of additional jobs in these companies:		**--**

18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:

☐	Increase in employment, or	☐	In small & medium-sized enterprises
☐	Safeguard employment, or	☐	In large companies
☐	Decrease in employment,	☒	None of the above / not relevant to the project
☒	Difficult to estimate / not possible to quantify		

19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (*FTE = one person working fulltime for a year*) jobs:	*Indicate figure:*
Difficult to estimate / not possible to quantify	☒

[11] Open Access is defined as free of charge access for anyone via Internet.
[12] For instance: classification for security project.

I	Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?

○ Yes ● No

21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?

● Yes ○ No

22 Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?

☒	Press Release	☒	Coverage in specialist press
❑	Media briefing	☒	Coverage in general (non-specialist) press
❑	TV coverage / report	❑	Coverage in national press
❑	Radio coverage / report	❑	Coverage in international press
☒	Brochures /posters / flyers	☒	Website for the general public / internet
❑	DVD /Film /Multimedia	☒	Event targeting general public (festival, conference, exhibition, science café)

23 In which languages are the information products for the general public produced?

☒	Language of the coordinator	☒	English
☒	Other language(s) (Czech)		

Question F-10: Classification of Scientific Disciplines according to the Frascati Manual 2002 (Proposed Standard Practice for Surveys on Research and Experimental Development, OECD 2002):

FIELDS OF SCIENCE AND TECHNOLOGY

1. NATURAL SCIENCES

1.1 Mathematics and computer sciences [mathematics and other allied fields: computer sciences and other allied subjects (software development only; hardware development should be classified in the engineering fields)]

1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)

1.3 Chemical sciences (chemistry, other allied subjects)

1.4 Earth and related environmental sciences (geology, geophysics, mineralogy, physical geography and other geosciences, meteorology and other atmospheric sciences including climatic research, oceanography, vulcanology, palaeoecology, other allied sciences)

1.5 Biological sciences (biology, botany, bacteriology, microbiology, zoology, entomology, genetics, biochemistry, biophysics, other allied sciences, excluding clinical and veterinary sciences)

2 ENGINEERING AND TECHNOLOGY

2.1 Civil engineering (architecture engineering, building science and engineering, construction engineering, municipal and structural engineering and other allied subjects)

2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]

2.3. Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as geodesy, industrial chemistry, etc.; the science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)

3. MEDICAL SCIENCES

3.1 Basic medicine (anatomy, cytology, physiology, genetics, pharmacy, pharmacology, toxicology, immunology and immunohaematology, clinical chemistry, clinical microbiology, pathology)

3.2 Clinical medicine (anaesthesiology, paediatrics, obstetrics and gynaecology, internal medicine, surgery, dentistry, neurology, psychiatry, radiology, therapeutics, otorhinolaryngology, ophthalmology)

3.3 Health sciences (public health services, social medicine, hygiene, nursing, epidemiology)

4. AGRICULTURAL SCIENCES

4.1 Agriculture, forestry, fisheries and allied sciences (agronomy, animal husbandry, fisheries, forestry, horticulture, other allied subjects)

4.2 Veterinary medicine

5. SOCIAL SCIENCES

5.1 Psychology

5.2 Economics

5.3 Educational sciences (education and training and other allied subjects)

5.4 Other social sciences [anthropology (social and cultural) and ethnology, demography, geography (human, economic and social), town and country planning, management, law, linguistics, political sciences, sociology, organisation and methods, miscellaneous social sciences and interdisciplinary , methodological and historical S1T activities relating to subjects in this group. Physical anthropology, physical geography and psychophysiology should normally be classified with the natural sciences].

6. HUMANITIES

6.1 History (history, prehistory and history, together with auxiliary historical disciplines such as archaeology, numismatics, palaeography, genealogy, etc.)

6.2 Languages and literature (ancient and modern)

6.3 Other humanities [philosophy (including the history of science and technology) arts, history of art, art criticism, painting, sculpture, musicology, dramatic art excluding artistic "research" of any kind, religion, theology, other fields and subjects pertaining to the humanities, methodological, historical and other S1T activities relating to the subjects in this group]