PROJECT FINAL REPORT

Grant Agreement number: NMP3-LA-2011-262840

Project acronym: DEMCAMER

Project title: **DE**sign and **M**anufacturing of **CA**talytic **ME**mbrane **R**eactors by developing new nano-architectured catalytic and selective membrane materials

Funding Scheme: Large-scale integrating Collaborative Projects

Period covered: **from** 2011-07-01 **to** 2015-06-30

Name of the scientific representative of the project's co-ordinator[1], Title and Organisation:

Dr. José Luis Viviente

Fundación TECNALIA Research & Innovation

Tel: +34-610767840 & 34-946430850

Fax: +34-946460900

E-mail: joseluis.viviente@TECNALIA.com

Project website¡Error! Marcador no definido. **address:** www.demcamer.org

---

[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

Content

4.1. Final publishable summary report

4.1.1. Executive summary

DEMCAMER is a 4 years project focussing on the development of novel catalyst materials and membranes for the validation of membrane reactors for four industrially relevant reaction systems, namely Water Gas Shift (WGS), Autothermal reforming of methane (ATR), Oxidative coupling of methane (OCM) and Fischer Tropsch synthesis (FTS).

The project brings together 18 partners covering the whole value chain, ranging from powder producers, to catalyst developers, membrane developers, reactor and system developers, service providers and end users.

New active, stable and selective catalysts have been developed within DEMCAMER for all the reaction system of interest and their production has been scaled up to kg scale (TRL5). At the same time new membranes for gas separation have been developed in the project; in particular, dense supported thin palladium based membranes have been developed for hydrogen separation from reactive mixtures These membranes have been successfully scaled up to TRL4 and used in various lab-scale reactors for WGS (using both packed bed and fluidized bed reactors) and FTS (using packed bed reactors) and in prototype reactors for WGS and FTS. Mixed ionic-electronic conducting membranes in capillary form have been also developed in the project for high temperature oxygen separation from air. These membranes can be used for both ATR and OCM reaction system to increase the efficiency and the yield of the processes. The production of these membranes has been scaled up to TRL3-4. Additionally, zeolite membranes have been developed for water separation and gas separation, although these membranes have not been validated in reactive conditions.

The project also developed adequate sealing techniques to be able to integrate the different membranes in lab-scale and prototype reactors.

Part of the project was devoted to multi-scale modelling of the materials and processes. At particle scale, DFT calculations have been used to evaluate and optimize the amount of active species in the catalysts. At membrane scale, phenomenological model have been used to evaluate and describe the permeation of gases through the membranes. Maxwell-Stefan approaches have been taken to better describe mass transfer limitations occurring in the boundary layer close to the membranes and inside the membrane pores. At reactor scale, both CFD and phenomenological models have been used to evaluate the reactor performances and optimize the operating conditions, while at system scale, flow-sheeting tools have been used to optimize the system performances.

Finally, four prototypes have been designed and constructed for the four reaction systems of interest. Of these prototypes, two based on Pd-based membranes have been successfully operated and the results can be used to validate the models and further develop the reactor design.

Of this large project, many of the milestones, especially on material (catalyst, supports, membranes) have been successfully achieved. Modelling and design milestones and construction of prototypes have been achieved as well. At larger scale the validation of all the processes was not possible for difficulties in membrane stability (especially the oxygen membranes).

4.1.2. Project context and objectives

Process Intensification (PI), which is defined as *"any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology"*, is already the next revolution of the chemical industry. The need for more efficient processes, including further flexible engineering designs and, at the same time, increasing the safety and environmental impact of these processes, is pushing the industry to novel research in this field. The chemistry and related sectors have already recognised the benefits of PI and estimate a potential for energy saving of about 1000 kilo tonnes of oil equivalent (toe) per year using these processes.

The technology of membrane reactor plays an important role in PI and is based on a device combining a membrane based separation and a catalytic chemical reaction in one unit. Every catalytic industrial process can potentially benefit from the introduction of catalytic membranes and membrane reactors instead of the conventional reactors. According to SusChem (European Technology Platform for Sustainable Chemistry, Strategic Research Agenda 2005) more than 80% of the processes in the chemical industry worth approximately €1,500 billion, depend on catalytic technologies, and one the shorter-term (5-10 years) objectives of this Platform is to *"integrate reactor-catalyst-separation design: integration and intensification of processes requires the development of new catalytic concepts which break down the current barriers (for example, low flux in catalytic membranes)"*.

The DEMCAMER project proposes an answer to the paradigm met by the European Chemical Industry: increase the production rate while keeping the same products quality and reducing both production costs and environmental impacts. Through the implementation of a novel process intensification approach consisting on the combination of reaction and separation in a "Catalytic Membrane Reactor" single unit.

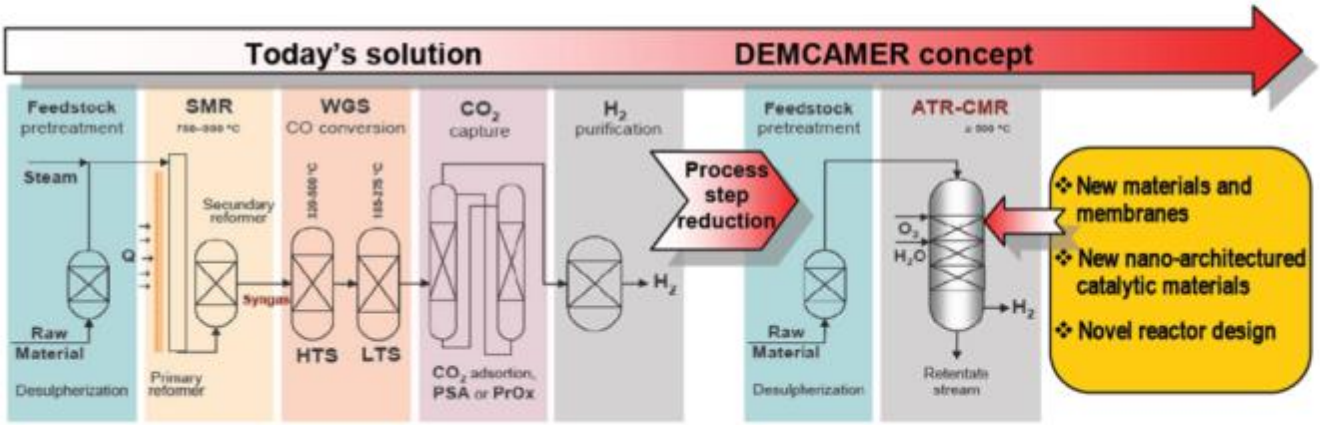

Figure 1. DEMCAMER project concept (ATR process)

The aim of DEMCAMER project was to develop innovative multifunctional Catalytic Membrane Reactors (CMR) based on new nano-architectured catalysts and selective membranes materials to improve their performance, cost effectiveness (i.e.; reducing the number of steps) and sustainability (lower environmental impact and use of new raw materials) over four selected chemical processes ((Autothermal Reforming (ATR), Fischer-Tropsch (FTS), Water Gas Shift (WGS), and Oxidative Coupling of Methane (OCM)) for pure hydrogen, liquid hydrocarbons and ethylene production.

The scientific and technical objectives to achieve this general objective were the following:

- Development of novel catalyst materials with enhanced properties for improved catalytic conversion of the considered processes:
  - A novel class of ATR catalysts based on perovskites generically represented by the formula $La_{1-x}Sr_xCr_yB'B''_yO_3$ where B' and B'' are selected from Ru, Fe, Mn, Co, Ni

  - WGS catalysts based on Pt alloys supported on modified ceria and titania with improved catalytic activity.
  - Development of OCM catalysts based on tungsten and promoted with manganese and rare earths and supported on conventional silica carrier.
  - FTS: core-shell type bimetallic nano-catalysts based on Ru@Co, Co@Ru and Co@Fe
  - Catalyst materials for each type of process obtained by POSS® nanotechnology.
- To develop new membrane materials with improved separation properties, long durability, and with reduced cost for catalytic reactors designed for gas and water separation (ATR, WGS, OCM and FTS)
  - Mixed ion electron conductive (MIEC) membranes (dense nanostructured coatings and hollow fibres) for O_2 and H_2 separation
  - Metal based membranes for H_2 production based on Pd-multi alloys and non-Pd alloys over the DOE target for 2015.
  - Zeolite membranes based on defect free NaA stabilised sodalite (SOD) and FAU membranes with entrapped catalytic nano-sized particles
- To understand the fundamental physicochemical mechanisms and the relationship between structure/property/performance and manufacturing process in membranes and catalysts, in order to achieve radical improvements in membrane reactors.
- To design, model and build up novel more efficient (e.g. reducing the number of steps) membrane reactor configurations based on the new membranes and catalysts supported by simulation.
- To validate the new membrane reactor configurations, at semi-industrial prototype level, in four selected chemical process (Autothermal Reforming (ATR), Fischer-Tropsch (FTS), Water Gas Shift (WGS), and Oxidative Coupling of Methane (OCM)) for pure hydrogen, liquid hydrocarbons and ethylene production.
- To improve the cost efficiency of membrane reactors by increasing their performance, decreasing the raw materials consumption and the associated energy losses.
- To enable the use of new raw materials (i.e.; convert non-reactive raw materials)
- To assess the health, safety and environmental impact of the four CRM developed processes, a complete LCA of the developed technologies will be performed

The DEMCAMER work plan consisted of activities related to the whole product chain: i.e. development of materials/components (membranes, supports, seals, catalyst...) through integration/validation at lab-scale, until development/validation of four semi-industrial pilot scale CMRs prototypes. Additionally, three research lines dealing with: 1) the collection of specifications and requirements, 2) modelling and simulation of the developed materials and processes, and 3) assessment of environmental, health & safety issues -in relation to the new intensified chemical processes- were also carried out.

For a maximum impact on the European industry this research, covering the complete value chain of catalytic membrane reactors, was carried out with a multidisciplinary and complementary team having the right expertise, including top level European Research Institutes and Universities (8 RES) working together with representative top industries (4 SME and 6 IND) in different sectors (from raw materials to petrochemical end-users).

The following figure and table summarised the four chemical processes addressed by DEMCAMER including the raw materials and products per each targeted reaction. Membranes for the different processes are also indicated in the flow sheet. Both the flow sheet and the table are not taking into account previous stages of pre-treatment for the raw materials as this will not be addressed in DEMCAMER.

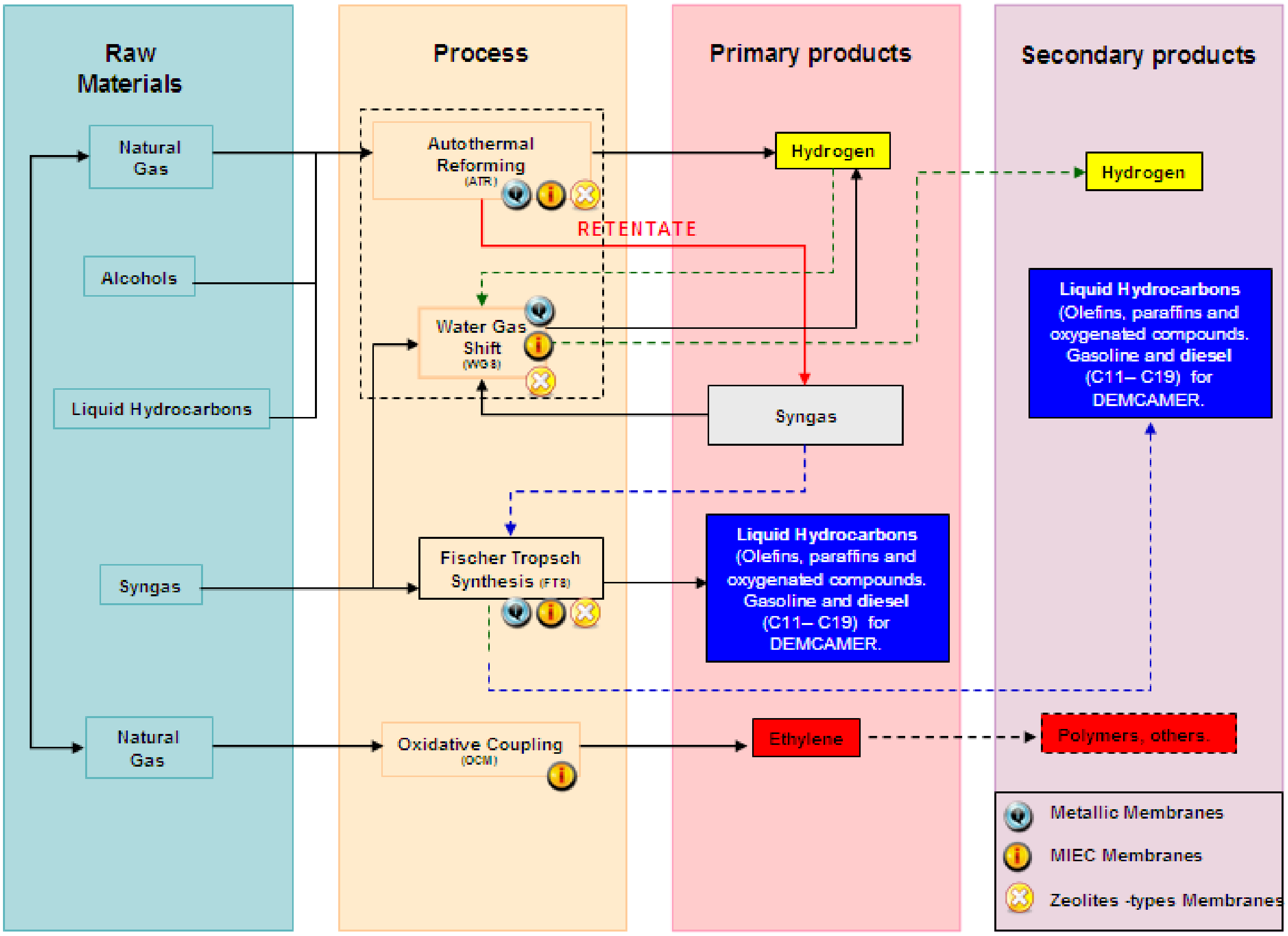

Figure 2. Flowsheet of the four chemical processes addressed in DEMCAMER.

Table 1. Raw materials and obtained products per each targeted reaction.

Process	Raw Materials (1)	Products (2)
ATR	**Natural Gas (mainly CH_4)**	**H_2**
	SNG (Synthetic Natural Gas produced from coal, biomass, petroleum coke, or solid waste)	
	Alcohols (Methanol & Ethanol)	
	Dimethyl ether (DME)	
	Liquid Hydrocarbons derived from fossil fuels (gasoline, diesel, naptha, etc.)	
	Biogas	
	Biofuels (biodiesel, bioethanol, etc.)	
WGS	**Syngas**	**H_2**
FTS	**Syngas**	Liquid Hydrocarbons: Olefins, paraffins and oxygenated compounds. Gasoline **and diesel (C_{11} – C_{19})**
OCM	**Natural Gas**	**Ethylene**
	SNG	
	Biogas	

(1) Highlighted text in black colour corresponds to raw materials used in DEMCAMER project.
(2) Highlighted text in black colour corresponds to products obtained in the DEMCAMER project.

Raw materials for the ATR process could be very wide: natural gas, SNG (Synthetic Natural Gas produced from coal, biomass, petroleum coke, or solid waste), alcohols (methanol & ethanol), Dimethyl ether (DME), liquid hydrocarbons derived from fossil fuels (gasoline, diesel, naphtha, etc.), biogas, biofuels (biodiesel, bioethanol, etc.). DEMCAMER was only addressing natural gas (mainly CH_4) as raw material. On the other side, Syngas could be the raw material for the WGS and the FTS processes. Syngas could be derived from dry, steam, partial oxidation and autothermal reforming processes using natural gas, coal or biomass. Finally, natural gas, SNG or Biomass could be raw materials in the OCM process but natural gas was the raw material considered in DEMCAMER.

On the other side, targeted primary products were H_2, liquid hydrocarbons (gasoline/diesel fractions (C_{11}-C_{20}) and ethylene. The definition and identification of the specific industrial requirements for the intensification of each targeted reaction has been addressed at the beginning of the project.

The DEMCAMER Project has been funded under FP7 Cooperation Specific Programme and Nanotechnologies, Materials and Processes NMP Theme. The Project has started the 1st of July of 2011 and it has run for 48 months

4.1.3. Main S&T results/foregrounds

The DEMCAMER project was finalised by end of June 2015. Many progresses have been achieved in all stages of the value chain, from development of the catalysts, membranes, through lab-scale validation, to pilot scale development and testing. Modelling of the technologies also covered a wide range in level of detail from ab-initio calculation for membranes and catalysts, transport in membranes and catalytic membrane reactors simulation to complete process design and simulation. Pilot scale reactors were designed and tested with to different extent for the different processes. Complete assessments of the health, safety and environmental impact of the four CRM have been also addressed. Main S&T results/foregrounds achieved at the end of the project are detailed hereafter.

4.1.3.1. Catalytic Materials

Beneficiaries involved in the development of catalytic materials have designed several catalysts for each process (more than 100 catalyst samples) addressed in the project (ATR, WGS, OCM and FTS). Selection of DEMCAMER catalysts has been completed from catalytic screening tests together with a deep characterization of fresh and used samples in order to know the main structural and surface characteristics of the catalysts developed in DEMCAMER that have strong influence on the catalytic activity and stability. For each catalyst generation the most optimal compositions, in terms of activity and stability, were selected, prepared and supplied for testing at laboratory scale. From durability tests in laboratory reactions, the final optimal composition was selected, with emphasis on the catalyst nanostructure control, as final catalyst generation for scale-up and conformation for testing at pilot scale.

Final catalyst generation developed for each processes showed improved activity, selectivity and stability over catalytic formulations described in the state of the art achieving for all processes, therefore, the initial DEMCAMER objectives. Main results are the following:

ATR catalyst
The integration of the ATR reactor with membrane requires the use of catalysts with extreme thermal stability (structural/morphological resistances) and high resistance to carbon formation and deactivation by sulphur. Taking into account that ATR catalyst poisoning by sulfur and/or carbon is a structure sensitive reaction, the control of the electronic structure and size of the active metal surfaces has been the strategy followed in the development of innovative ATR catalysts with improved catalytic activity and stability. The ATR catalysts developed in DEMCAMER have been designed following two alternatives: the first, more innovative, based on catalysts with spatially distributed active metal components in a stable structure under reaction conditions and the second, more conventional, based on the modification of supported active metal clusters via the presence of other metals. Within the first alternative a novel class of ATR catalysts based on perovskites generically represented by the formula $La_{1-x}Sr_xCr_yB'B''_yO_3$ where B' and B'' are selected from Ru, Co, Ni, have been studied in DEMCAMER project. The second class of ATR catalyst was based on more conventional supported catalysts studying different ATR catalysts series varying the nature of active phase (Ni, Ru, Pt, Pd), the support (La_2O_3, CeO_2-ZrO_2, CeO_2-Gd_2O_3) and the method of preparation (impregnation, sol-gel,…). Selection of ATR catalysts has been completed from catalytic screening in the ATR reaction of methane at laboratory level together with a deep characterization of fresh and used samples of all catalytic series prepared. The main structural and surface characteristics of the catalysts that have strong influence on the ATR catalytic activity and stability have been identified. From catalytic screening tests, durability tests and characterization of ATR catalysts, the optimal composition and preparation method of catalyst was selected. The final generation of ATR catalysts developed in DEMCAMER was based on Ni-Pd catalysts deposited on optimized ceria based support. The ATR catalyst developed at DEMCAMER showed very high activity/stability in the ATR reaction through: i) the control of synergistic Ni-Pd interaction and ii) optimization of the oxygen storage capacity of the cerium based support. The final generation of ATR catalyst showed activity, selectivity and stability in compliance with the DEMCAMER targets (Table 1).

Table 2. Compliance of ATR catalyst developed in DEMCAMER with the requirements of activity, selectivity and durability.

	X_{CH4}, %	S_{H2},%	TOS, h	$T_{reaction}$, ºC	GHSV, h^{-1}	O_2/C	H_2O/C	C_{H2S}, ppm
Objective	90	60	100	750-900	20000-80000	0.2-0.7	3-5	50
DEMCAMER ATR catalyst	100	80	100	850	22500	0.75	1	50

The ATR catalyst showed stable performance (methane conversion > 90%, hydrogen yield > 80%) and resistance to deactivation by sulphur and coke during 100 h of operation under reaction feed containing 50 ppm of H_2S (Figure 3). Characterization of used catalysts showed excellent resistance to deactivation by carbon formation (no carbonaceous deposits on used catalyst).

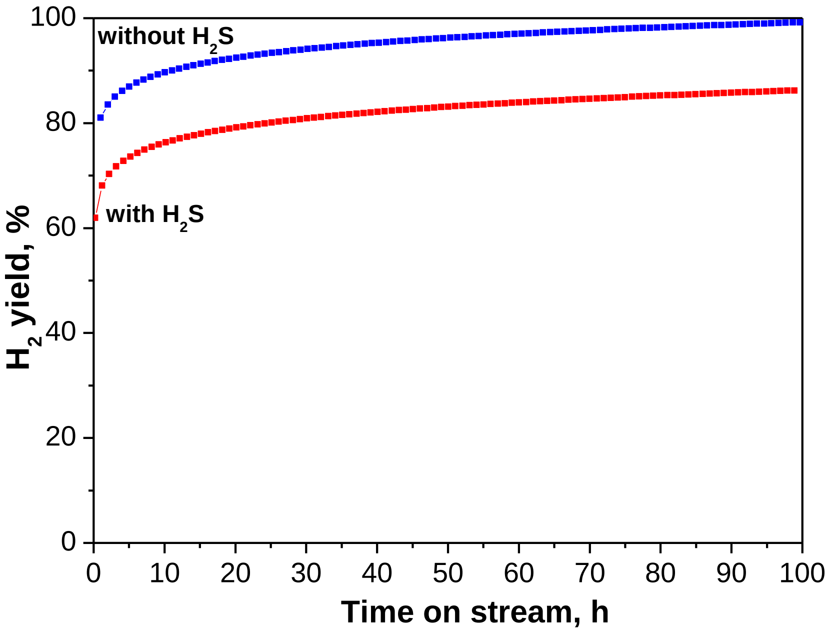

Figure 3. Long term catalyst testing in ATR of CH_4 (T=850º, CH_4:H_2O:O_2=1:2,5:0.75) of ATR catalyst developed in DEMCAMER project.

WGS catalyst

The application of WGS catalysts in membrane reactors needs extensive research with the objective to improve catalyst activity, selectivity and stability since the membrane reactor conditions are very different from those encountered in a conventional shift reactor (temperature limit due to membrane stability, low partial pressure of steam and high partial pressure of CO_2). In the development of WGS catalysts, innovative WGS catalyst formulations based on ceria and titania-based platinum catalysts have been studied in DEMCAMER project. In order to improve the WGS activity of catalysts two different strategies have been studied: (i) the modification of the electronic structure of the Pt metal surfaces by alloying surface Pt with other atoms and (ii) the modification of ceria and titania supports with basic or acidic dopants to promote redox sites for water dissociation during WGS reaction. Taking into account that the activity of Pt catalysts supported on TiO_2 based supports is associated to the formation of Pt-support interfaces producing oxygen vacancies, it is clear that the preparation method of the WGS catalysts must also be controlled selecting methods that promote the formation of interfaces between Pt metal and support surfaces. Conventional preparation method based on controlled impregnation has been applied in order to tune both the Pt-support interactions and the type of Pt surface species (small metal clusters, Pt ions and Pt atoms at a metal cluster edge) present on catalyst surface. Selection of WGS catalysts has been completed from catalytic screening in the WGS reaction at laboratory level together with a deep characterization of fresh and used samples. From catalytic WGS screening tests and physico-chemical characterization data, the optimal composition and preparation method of WGS catalyst was selected. The final generation of WGS catalysts developed in DEMCAMER was based on Pt-Re catalysts deposited on optimized cerium-titanium mixed oxide support. The WGS catalyst developed in DEMCAMER project showed very high WGS activity and stability, showing an important improvement respect to the state-of-the art FeCr HT WGS commercial catalyst (Figure 4).

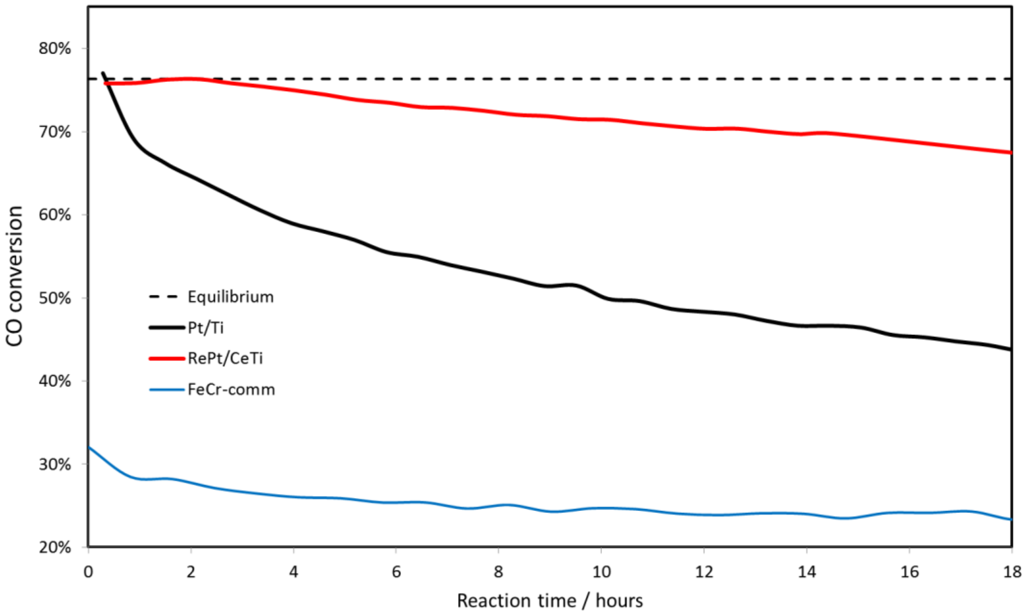

Figure 4. Comparison of CO conversion over the WGS catalyst developed in DEMCAMER and state-of-the-art Fe/Cr catalyst.

OCM catalyst

The integration of the OCM reactor with mixed ionic-electronic conducting membranes (MIECM) requires a good match between oxygen permeation rate through membrane and the OCM reaction rate on catalyst. The La-Sr/CaO and Mn-Na_2WO_4/SiO_2 type catalysts were shown to be among the most suitable for OCM reaction, and therefore they have been used as base formulations to be optimized after a systematic synthesis, physicochemical and catalytic characterization studies in DEMCAMER project. The OCM catalysts developed in DEMCAMER have been designed following two strategies to improve OCM activity/selectivity/stability: (i) optimization of formulations and oxide contacts by application of different preparation methods and (ii) addition of dopants (Mn and rare earths) and promoters (S, P, Cl) to increase the selectivity to ethylene. At the first stage of the investigation, the optimal support type and value of metal content for Mn-Na_2WO_4/SiO_2 OCM catalysts were established. Further, the modification of Mn-Na-W/SiO_2 material by different promoters as structural and electronic modifying agents was performed. From these results, Mn-La- modified-Mn-Na_2WO_4/SiO_2 OCM catalysts was selected as more perspective composition. The optimization of preparation techniques (incipient wetness impregnation, mixture slurry method), conditions of impregnation (temperature of impregnating solution), temperature of catalyst calcination (800ºC, 850ºC, 900ºC, 1000ºC) and pretreatment conditions of Mn-Na_2WO_4/SiO_2 catalyst before OCM reaction (700ºC O_2/He; 800ºC O_2/He; 800ºC He) were also optimized. The optimal OCM catalyst derived from DEMCAMER project (Figure 5) provide high activity/selectivity (CH_4

conversion=55%, C_2 yield=22%) close to the best results in the state-of-the-art through i) optimal active phase exposition and ii) surface phase stability at high temperature.

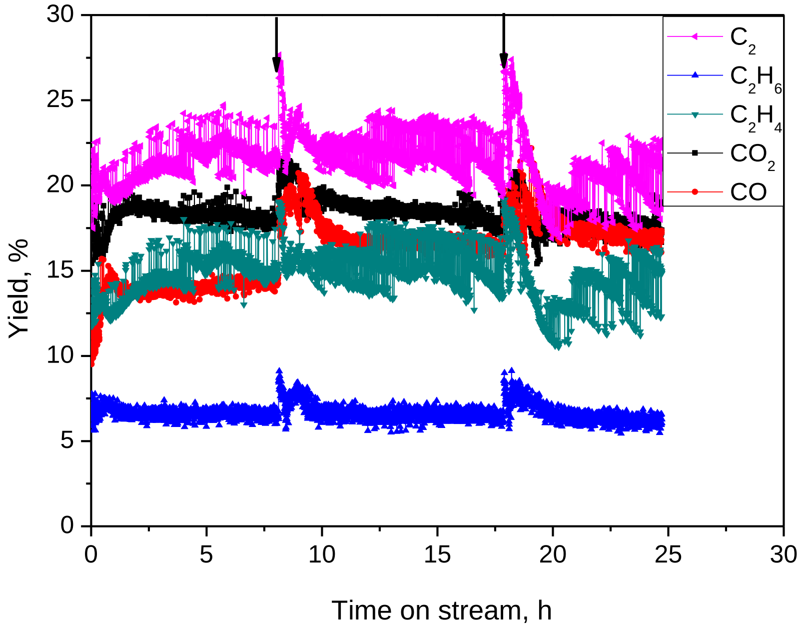

Figure 5. Long term catalyst testing in OCM reaction (T=800ºC, O_2/CH_4=2/4 GHSV=22500 h^{-1}) over OCM catalyst developed in DEMCAMER project

FTS catalyst

The use of membrane reactors for FT reactions is an attractive option because this approach allows to control the heat of the reaction and to enhance the selectivity to long-chain hydrocarbons. Several concepts such as distributed hydrogen feed, water removal and forced-through flow membrane have been assessed using different reactor configurations. FTS membrane reactors require the integration of novel catalysts with higher catalytic performances that that of state-of-the-art Co-based catalysts in terms of C5+ productivity. To achieve this objective, several generations of FTS catalyst based on Ru-type have been prepared, characterized and tested for the FTS reactor in DEMCAMER project. The strategies followed in DEMCAMER project to improve activity/selectivity of FTS catalysts were: (i) the synthesis of core-shell ruthenium-containing bimetallic nanostructured catalysts of the type Ru@Co, Ru@Fe and Ru@Ni, (ii) the use of TiO_2 as support to control the exposition and interaction of Ru active sites and, (iii) the addition of promoters (B) to increase the stability and selectivity to C5+. The first generation of FTS catalysts consisted in Al_2O_3 supported bimetallic particles M/Ru (M=Fe, Co or Ni) with core@shell (M@Ru) like structures. Based upon foreground knowledge other generation of FTS catalysts were also developed based upon B-doped Ru/TiO_2. From catalytic screening FTS tests, durability tests and characterization of catalysts, the optimal composition and preparation method of FTS catalyst was selected. We succeed in preparing Co@Ru and Ru/TiO_2 catalysts with very high FTS performances with initial and steady-state CH_2 production rates of ca. 180 and 120 $mol_{CH2}/h/at\text{-}gr_{Ru}$, respectively. In addition we found that the presence of B in B-Ru/TiO_2 prevents catalyst deactivation by suppressing the formation of carbon deposits during the FTS reaction. The catalyst formulation B-Ru/TiO_2 was selected as final generation catalyst achieving over this catalyst high values of activity, selectivity and stability in compliance with the DEMCAMER targets (Table 3). It should be mentioned that hydrocarbon productivity with the final FTS catalyst formulation was higher than that reported for the benchmark Co-based and also identified in the industrial requirements for the intensification of targeted FTS reaction.

Table 3. Compliance of FTS catalyst developed in DEMCAMER with the requirements of activity and selectivity.

	X_{CO},%	C5+ sel	$T_{reaction}$, °C	Pressure, bar	H_2/CO
Objective	>50	>40	< 300ºC	20-30	2
DEMCAMER FTS catalyst	60	60	235	20	2

The B-Ru/TiO_2 FTS catalyst developed in DEMCAMER project achieves a CO conversion above 60% maintained for up to 80 h on stream (Figure 6).

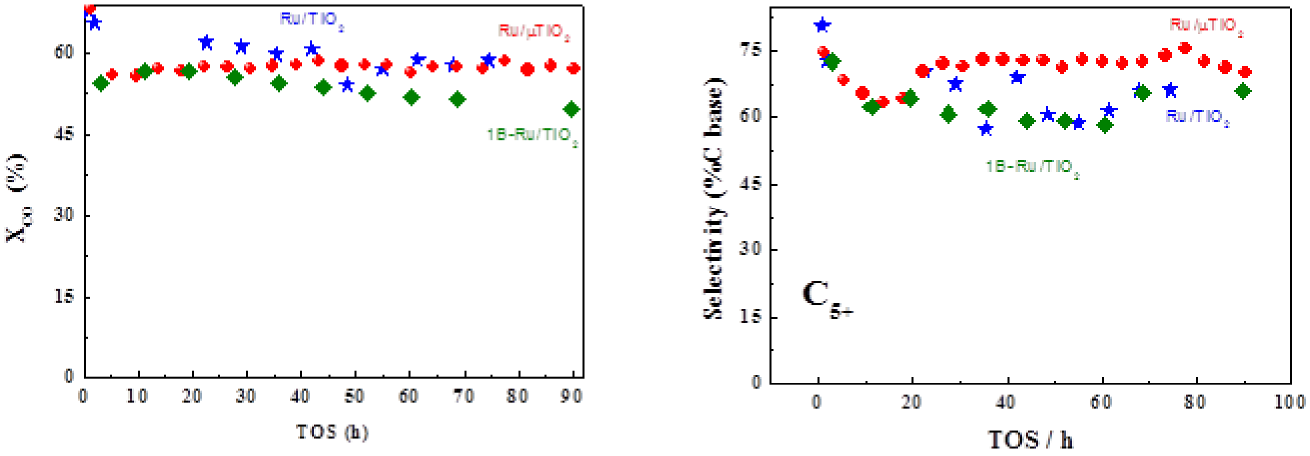

Figure 6. CO conversion (left panel) and selectivity to C_{5+} (right panel) with Ru/TiO_2, 1B-Ru/TiO_2 and Ru/µ-TiO_2 at H_2/CO=2, 523 K, 7500 mL $H_2/CO \cdot g^{-1}$ cat $\cdot$ h^{-1}. 20 bar.

4.1.3.2. Membranes

Beneficiaries involved in membranes have developed and supplied the membranes for the ATR, WGS, OCM and FTS lab-scale catalytic membrane reactors and pilot prototypes. The first part of the work has been devoted to the development of the materials for the Mixed Ion-Electron Conducting membranes, zeolite membranes, metallic supports and interdiffusion layers and selection of improved materials for the target application. Afterward, a selection has been made for the most promising ceramic and metallic porous supports as well as the interdiffussion barrier layers and of the improved membrane materials. Finally, the different membranes MIEC, metal based membranes for H_2 separation and zeolite membranes for FTS were developed. Best membranes were selected for the pilot scale reactor after testing at lab-scale. Main results end of the project are detailed hereafter.

MIEC membranes

Screening production of feedstock perovskite powders for the development of hollow fibers for O_2 and H_2 permeation has been carried out. Protocols for large-scale production (Figure 7) of the selected perovskite material have been set up. MIEC hollow fibers were developed by spinning and phase inversion methods (Figure 8). Following the lab-scale permeation tests O_2 MIEC membranes have been selected for the prototype. For ATR and OCM more than 80 MIEC membranes in lengths of 10 cm and more than 40 in lengths of 5 cm have been produced and made available. However, when sealed did not have sufficient mechanical integrity to withstand mechanical stresses during the integration in the reactor prototype assemblies.

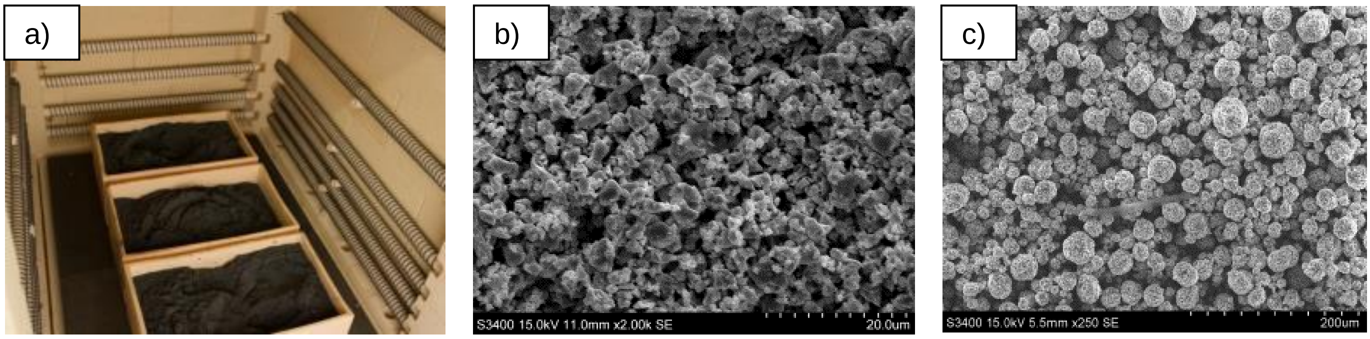

Figure 7. a) Scale up production; b) Morphology before freeze granulation process and c) Morphology after freeze granulation process.

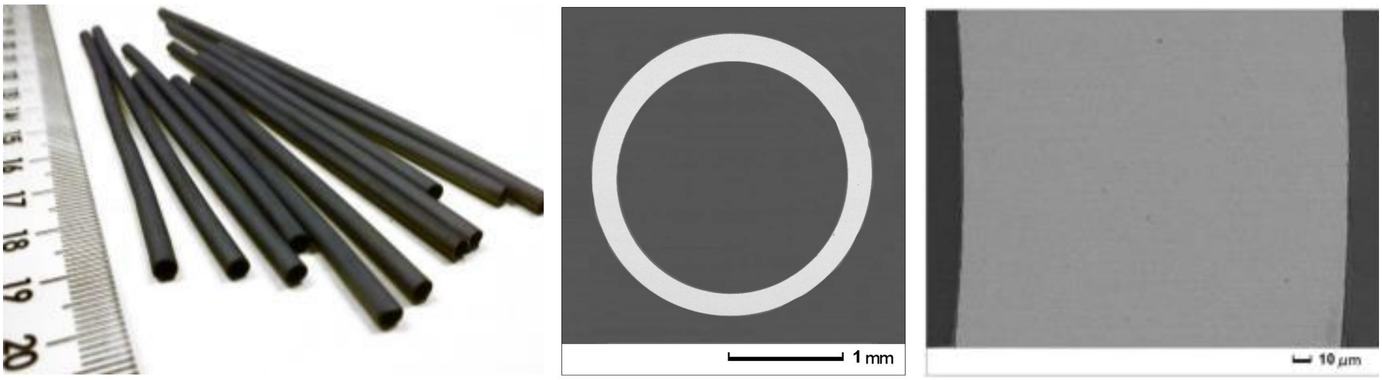

Figure 8. MIEC hollow fibers for O_2 permeation.

In addition MgO porous supports have been also developed. They could be used as supports for the development of MIEC supported membranes

Metal based membranes for H_2 production

Both metal based and ceramic based porous supports (Al_2O_3, TiO_2, Mullite) have been developed in the frame of the DEMCAMER project (Figure 9).

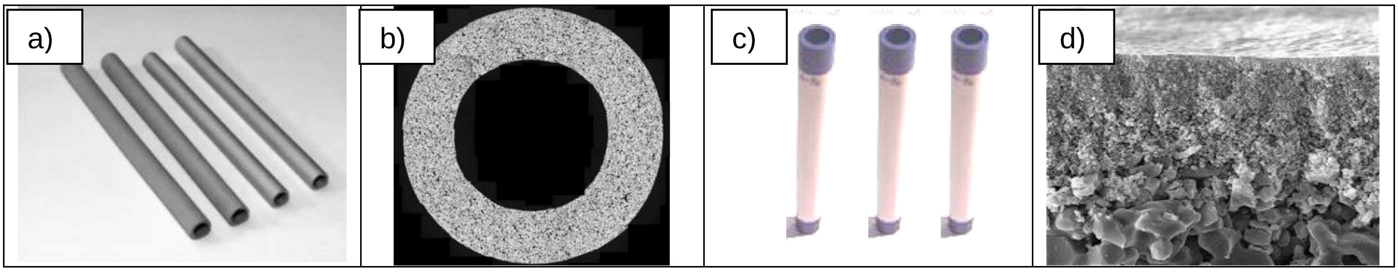

Figure 9. a) Metal porous supports, b) Cross section of a metal porous support, c) Ceramic porous support (50 cm long) and d) Cross section of the external side of the ceramic porous support showing the 100 nm pore side Al_2O_3 top layer).

To increase the mechanical properties of the ceramic Al_2O_3 porous supports thicker walls porous supports has been developed. Figure 10 shows the improved properties of the 1 channel porous supports when increasing the wall from 1.5 to 3 mm (1-ch. tube OD 10 mm / ID 7 mm and 1-ch. tube OD 10 mm / ID 4 mm).

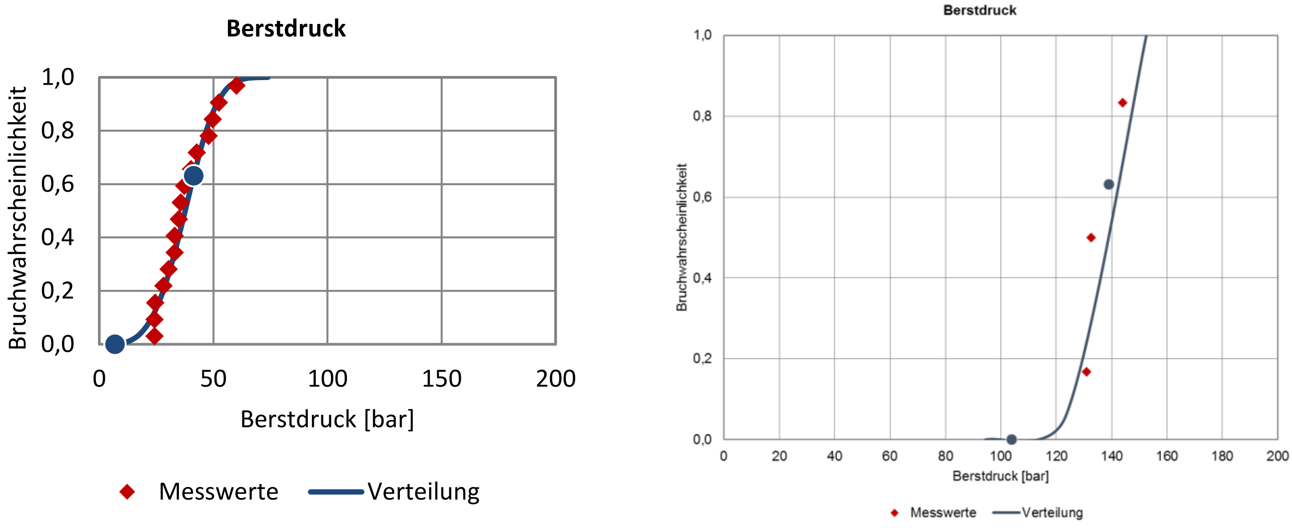

Figure 10. Left: Weibull of last batch 1-ch.-tube OD10*ID7. Right: Weibull of samples 1-ch.-batch-tube OD10*ID4.

Pd-Ag membranes supported onto Al_2O_3 porous ceramic support have been developed by simultaneous electroless plating showing H_2 permeances (>2.6 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1}) and selectivities (H_2/N_2 > 10,000) over the DEMCAMER target. Besides the membranes for the lab-scale tests, 33 membranes of 22-23 cm long (OD 10 mm – ID 7 mm) have been delivered for the WGS prototype. In addition, 5 Pd-Ag membranes of 15 cm long (OD 10 mm – ID 7 mm) with higher Ag content have been developed by a two-step process: simultaneous electroless plating of Pd-Ag and direct Ag deposition by PVD. These membranes have been delivered for testing the FTS H_2 distributed feeding concept at small pilot scale.

Figure 11. Left: Cross section of a Pd-Ag membrane. Right: Pd-Ag membranes to be integrated in the lab-scale reactor.

Zeolite membranes

Zeolite membranes were made as a thin layer of NaA, MFI and S-SOD inside of porous ceramic α-Al_2O_3 tubes (prepared by RKV) by a stepwise synthesis for water separation in FTS-CMR. Alongside this a carbon (C) membrane was developed and tested for this purpose. By end of the project, S-SOD did have low water selectivity because of a high defect rate and NaA was non stable in the test conditions. However, MFI and Carbon membranes show water separation properties suitable to be used for testing the water separation concept in FTS.

Table 4. Results of H_2O/gas mixed gas permeation test of different membranes prepared inside of ceramic tubes.

Membrane	**T [°C]**	**P_{feed} [bar]**	**P_{feed} [bar]**	**gas**	**p_{H2} [$m^3/(m^2 \cdot h \cdot bar)$]**	**$\alpha_{H2O/gas}$**
S-SOD	200	4	1	N_2	30	4
NaA	200	11	1	N_2	8	∞
MFI	200	11	4	N_2	6	∞
	200	11	4	H_2	6	300
	200	11	4	CH_4	6	560
	200	11	4	CO_2	5	70
Carbon	150-280	8-11	1	N_2	6-18	∞
	150	11	1	H_2	8	130
	200	11	4	H_2	24	∞
	250	11	1	CH_4	6	∞
	150	11	1	CO_2	6	200

4.1.3.3. Lab-scale reactors

The beneficiaries involved on lab scale testing have designed, developed, construct and test different membrane reactors for the four reaction systems considered in DEMCAMER. The first part of the work has been devoted to the integration of catalyst and membranes in the new reactors. Particular attention has been paid to the selection of adequate sealing techniques that allow integration of the membranes without losing the membrane selectivity. Important was also the scalability of the sealing technique used. The most important results were related to the sealing of Pd-based membranes. Starting from very simple glass sealing we develop a system based on Swagelok/graphite that was scaled up to easily integrate tens of membranes in a single prototype. The latest results showed that this sealing could be used in WGS conditions achieving high purity of H_2 (with lower than 20 ppm CO). As for the oxygen membranes both gold/ceramic and reactive air brazing (based on silver/copper) have been successfully demonstrated. An important lesson learned during DEMCAMER is to check the compatibility of the catalyst material with the membranes. We developed a protocol to test the membranes and catalyst very early in the phase of development and avoid problems with interaction between the two.
In the following few highlights are reported for the four reaction systems.

Lab scale WGS
The WGS packed bed membrane reactors were designed and built for hosting Pd-based membranes produced in the DEMCAMER project as well commercial ones. These membrane reactors were used in by considering three different combinations of membrane and catalyst:

a) Pd-Ag supported membrane + catalyst developed in the DEMCAMER project.
b) Pd-Ag supported membrane developed in DEMCAMER + commercial catalyst.
c) Pd-Ag commercial membrane + catalyst developed in DEMCAMER.

The combination of catalyst developed in DEMCAMER with thin (thickness 3.6 micron) Pd-based membrane resulted in a significant drop (98%) in membrane permeance, probably owing to interactions between membrane and catalysts. To overcome this drawback, a commercial catalyst was used with another membrane developed in DEMCAMER with the same characteristics of the previous mentioned and it was not observed any significant drop in performance. In addition, the combination between a Pd-Ag commercial membrane (100 micron thick) and the DEMCAMER catalyst did not show any drop in the membrane permeance. The membrane permeation properties were evaluated both with and without a catalytic bed, before and after reaction experiments. The measurements were carried out up to 6 bar at 360 and 400°C. No influence of catalyst presence and thermal cycles on membrane permeation properties was observed for the whole experimental run which lasted more than 2100 hours. The MR performance, also compared with simulation model developed in WP8 with a satisfactory agreement, resulted among the best in literature in terms of both CO conversion and hydrogen recovery (96% CO conversion and 84% H_2 recovery @ 400 °C, 4 bar and a gas hourly space velocity of 2500 h^{-1}. In parallel, concentration polarization measurements were also performed on the same reactor, confirming a polarization of ca 25% as mean value, occurring in the reactor.

In addition, very extensive validation tests of fluidized bed membrane reactors have been achieved in the project. We tested both commercial and DEMCAMER membranes for both single tube and multi-tube configurations and with different catalysts. Lately we integrated 5 Pd-based membranes in the reactor and operated continuously for up to 800 h. The results reported in Figure 12 show that even in fluidization conditions the system is able to achieve flux and selectivities well above the DEMCAMER targets.

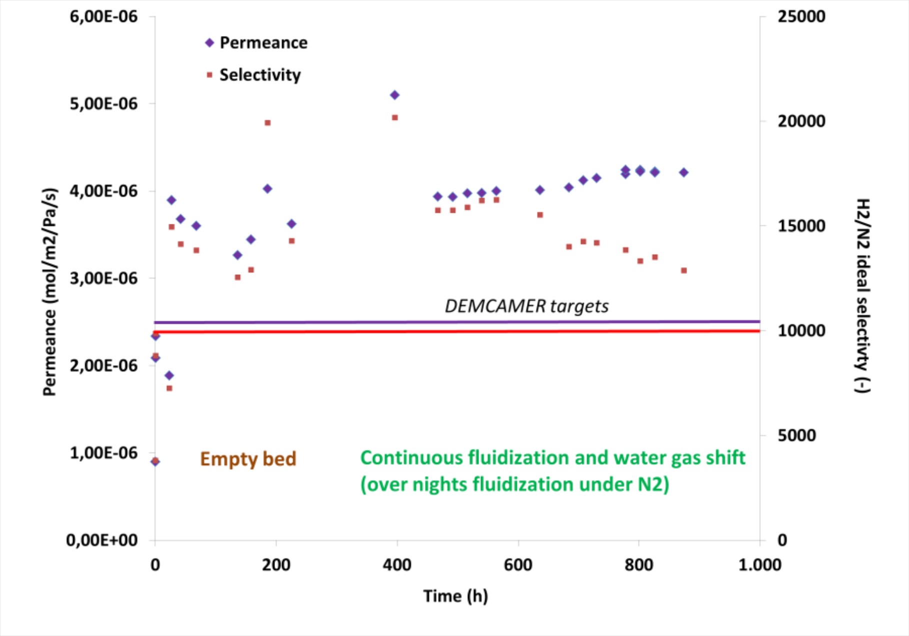

Figure 12. Experimental results in fluidized beds (H_2 permeance and H_2/N_2 ideal selectivity).

Best results show CO levels in the permeate side at levels of 5-7 ppm, which means that the produced hydrogen (recovered up to 60% in these tests) could be directly used in fuel cells. Additionally the catalyst does not react with nor stick to the membrane surface. These results fully demonstrate the WGS reactor concept.

Lab Scale OCM

A setup for OCM was built and the reactor demonstrated at lab scale. During the course of this final work on lab scale OCM CMRs the BCFZ hollow fibres used in different configurations often showed fractures along their length, most frequently in the sealing/contact zone. It is suspected that the main cause for this happening was the difference in thermal expansion coefficients (TEC) between the various components. Two types of catalyst materials obtained have been investigated for integration into the lab-scale OCM-CMR reactors 2wt.%Mn1.6wt.%Na3.1wt.%W/SiO2 and 2wt%Mn 1.6wt%Na 3.1wt%W 2wt%La/SiO2 (the latter being the third and final catalyst generation produced in DEMCAMER). Figure 13 shows a comparison of three schematic representations of the OCM CMR with different packing distribution of both above mentioned catalyst types. The catalyst was packed whether inside the membrane or outside the membrane inside a quartz tube.

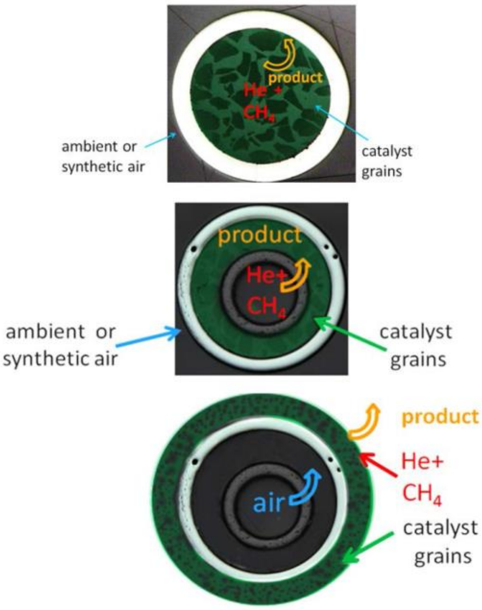

Figure 13. Three types of packed bed configurations that were explored: catalyst powder was contained within the constraints of the membrane (top and middle illustration) and catalyst powder filled up the space outside the membrane in a surrounding quartz tube (bottom). The latter two show the interior tube inside the membrane used for the sweep gas supply to the inside of the system.

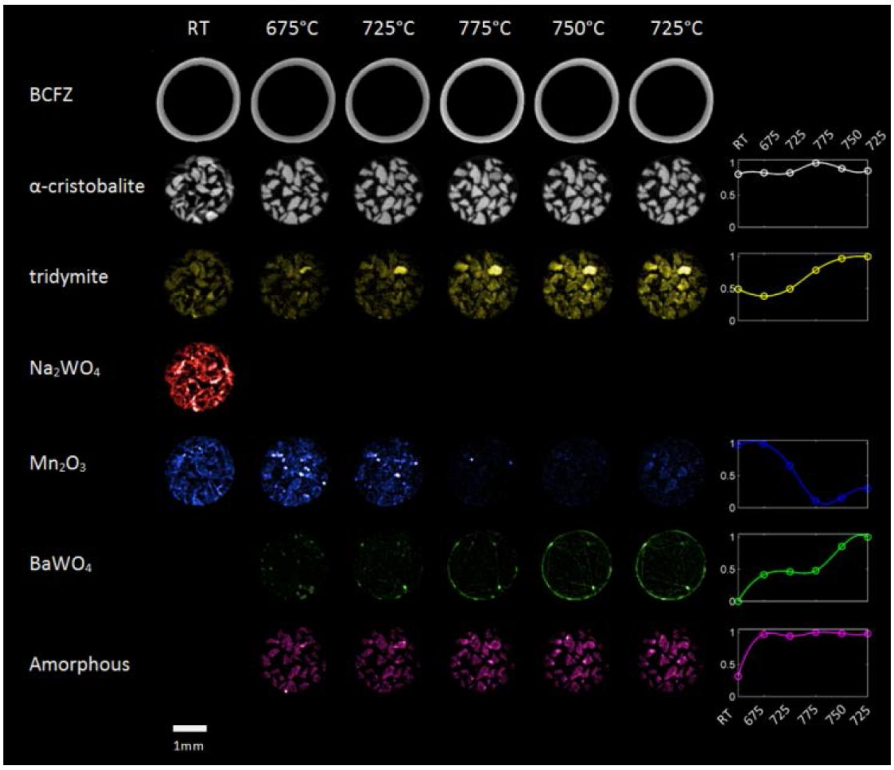

Figure 14. Phase maps obtained from the XRD-CT data (integrated intensities) of the BCFZ membrane phase and the catalyst phases: cristobalite and tridymite (SiO_2 polymorphs), Na_2WO_4, Mn_2O_3, Ba_2WO_4 and an amorphous phase.

Figure 14 shows the evolution of the CMR as the OCM experiment proceeds, presented as distribution phase maps of five identified crystalline phases and one amorphous phase of the catalyst and an intensity map of the (100) BCFZ reflection at temperatures where XRD-CT data are measured.

Typical outflow gasses monitored by mass spectrometry during these in situ XRD-CT measurements are shown in Figure 15. The gas product analysis with mass spectrometry was not fully quantified but it can serve to illustrate that the integrated reactor system was captured in its active state and the higher hydrocarbon molecules than CH4 have been detected

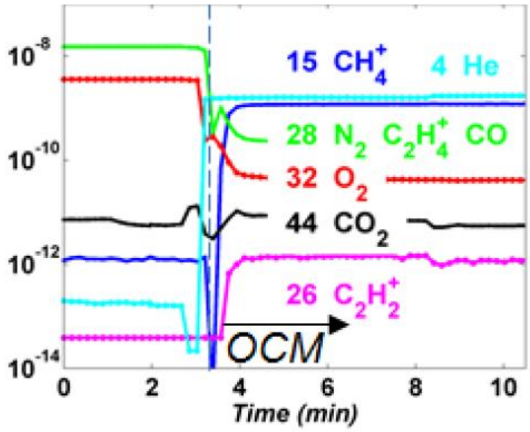

Figure 15. Mass spectroscopy data that correspond to the following masses: 4 (He - cyan), 15 (CH_4 - blue), 28 (N_2, CO, C_2H_4+ - green), 32 (O_2 - red), 44 (CO_2 - black) and 26 (C_2H_2+ - magenta).

Lab scale ATR

Based on the permeation results on membrane sealing and experimental permeation tests at high temperature, first a few membranes have been tested for long term testing.

The best results have been obtained with a BSFZ membrane, with high fluxes and good stability for more than 1000 hr. An example of such experiment is reported in Figure 16. In the Figure it can be seen that after a fist activation period of around 50 hr (due to adjustments in the lattice structure of the MIEC) the membrane flux remain very stable even after repeated cooling down and heating up of the system.

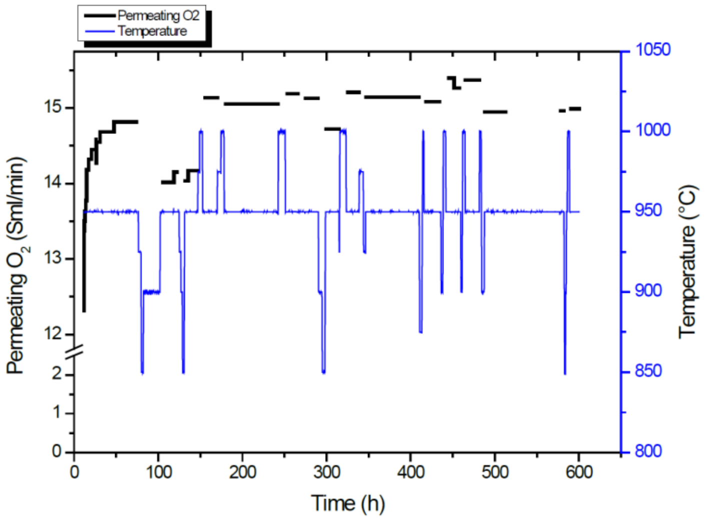

Figure 16. Permeating O2 flow rate in the outlet of the perovskite membrane reactor with 0.5 mm thickness, permeate side. He flow: 100 ml/min, Air flow = 500 ml/min.

Based on these promising results, a new membrane reactor for real validation has been designed and built. The reactor can accommodate 4 MIEC membranes with diameter of up to 4 mm and 10 cm length, and two porous membranes for steam addition. A schematic view of the new reactor can be seen in Figure 17.

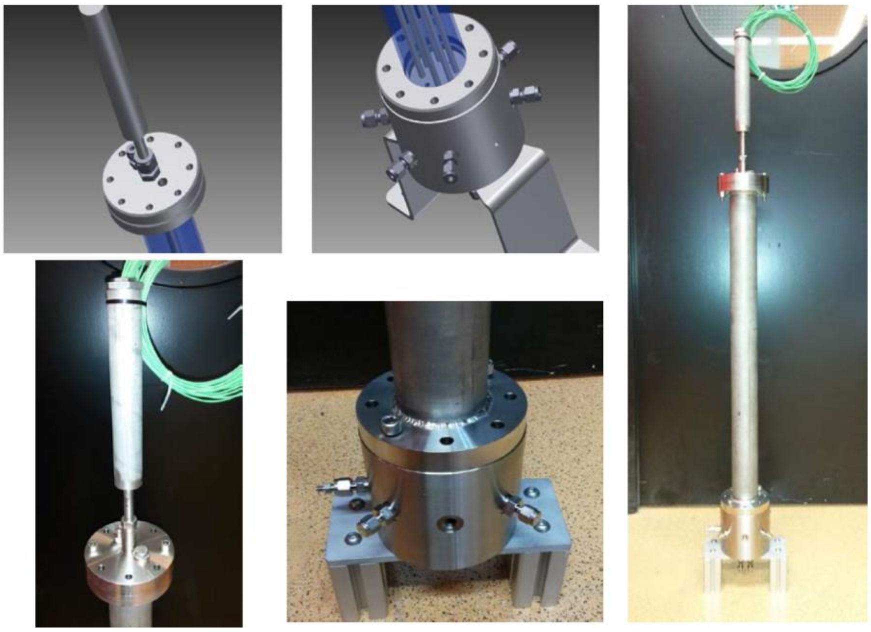

Figure 17. Parts of the new reactor as designed and built and final reactor assembled.

Unfortunately, the new batches of membranes received were of a lower quality compared with the original ones. Most of these membranes just broke while applying the first layer of the sealing.

Lab Scale FTS

The evaluation of the PBMR H_2-distributed feeding concept was also tested with Pd-Ag membranes developed in DEMCAMER. These membranes consist of a Pd and Ag layer (few microns) deposited at the outer layer of a ceramic tube. Both membranes have a length of Pd-Ag layer of 6 cm prepared over alumina tube with OD and ID of 10 and 7 mm. The FT catalyst used in all experiments with PBMR was the “final generation” FTS catalyst Ru-1B-Ti.

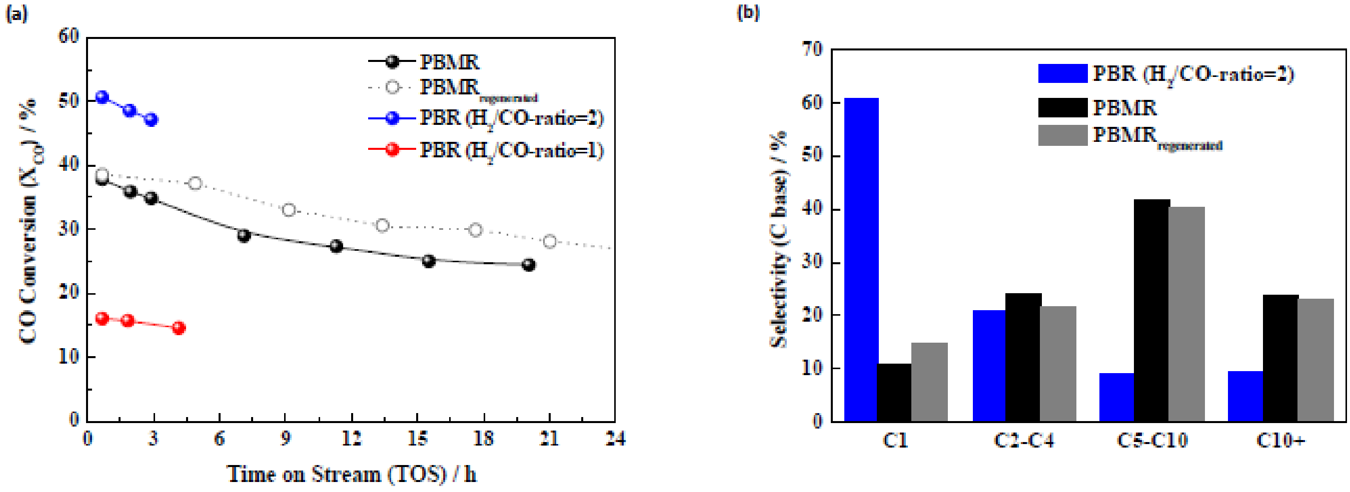

Figure 18. a) CO conversion at 280 ºC *vs*. time-on-stream for the following configurations: PBMR (H_2/CO=1) inside (black line), PBR H_2/CO=2 (blue line) and PBR H_2/CO=1 (red line) at P=10 bar, GHSV=7500mL$_{CO+H2}$/g$_{cat}$/h; ΔP^i_{H2}=9 bar. b) Product selectivity.

The most successful approach resulted when poor H_2 syngas (H_2/CO=1) was flown to the reaction chamber (inner side of the membrane) and the H_2 needed to reach the right FTS stoichiometry (H_2/CO=2) was admitted (and properly distributed) into the reaction chamber through the Pd-based membranes by flowing H_2/He at the outer side of the membrane. As shown in Figure 18, under the optimum reaction conditions (280 ºC), CO conversion recorded with the H_2-distributed feeding PBMR concept for FTS with $(H_2/CO=1)_{inner}$ is lower than that obtained in a conventional PBR feed with H_2/CO =2 (37.9 vs 50.7 %) but significantly higher than that obtained in a conventional PBR feed with H_2/CO =1 (14.1 %). Remarkably, product selectivity is positively affected by the "*more adequate*" H_2-distribution attained in the PBMR and the selectivity towards the targeted high-molecular hydrocarbons increases by a factor of 4. In addition, a significant decrease of CH_4 production (from 60 to 15%) is also observed (when compared to PBR at 280ºC). Under the studied experimental conditions membranes tend to deactivate after a few hours on stream (probably due to the formation of waxes) but their performance can be recovered by in situ thermal treatments under inert atmosphere.

4.1.3.4. Pilot scale prototypes

Pilot scale prototypes have been designed and assembled for each of the four industrial processes in DEMCAMER.

ATR

The autothermal reforming membrane reactor (ATR-MR) uses MIEC membranes to feed oxygen into the catalytic bed for reforming reaction. Oxygen is distributed along the reactor bed which reduces the temperature peaks compared to pre-mix feed. The reactor holds up to 80 membranes for oxygen feed. The reactor includes an auxiliary burner which is used for start-up and can also be used during operation to reach maximum production capacity of 5 Nm^3/h of hydrogen in syngas. Compared to conventional ATR the system in DEMCAMER does not require the supply of pure oxygen, which for small scale plants becomes economically unfeasible considering cryogenic separation of air.

Following the construction of the ATR prototype the factory acceptance tests have been carried out (including HAZOP: Hazard and Operability). In parallel, a test protocol for the Autothermal Reformer Membrane (ATR-MR) prototype was defined. The FAT showed leakage from each bundle equipped with membranes. Due to failure of overall installed membranes, it was not possible provide the oxygen required for the autothermal operating condition. The system, therefore, has been operated and tested as a natural gas steam reformer. During the testing (ca. one week) the system was stable and allowed produce up to 3.3 Nm3 of H2 per Nm3 of NG feed. The novel developed catalyst exhibited good activity and stability: test results showed almost complete conversion (>99 %) and hydrogen productivity higher than 90%.

At the current point in time the DEMCAMER technology applied to the ATR reaction has failed to deliver results beyond the laboratory scale. Significant improvements would have to be made on the robustness of the MIEC membranes before any industrial application under safe conditions could be imagined.

WGS

The pilot prototype is designed for producing 5 Nm^3/h grade 3.0 pure hydrogen in a water gas shift membrane reactor. The reactor separates hydrogen in-situ right where it is produced by means of WGS reaction. The complete setup includes the steam methane reformer which feeds the membrane reactor with real syngas rather than simulated gas from cylinders. Such setup allowed to evaluate the integration and definition of controls under realistic conditions.

Following the construction of the WGS prototype the factory acceptance tests have been carried out (including HAZOP: Hazard and Operability). In parallel, a test protocol for the Water Gas Shift Membrane Reactor (WGS-MR) prototype was defined.

The testing and validation of the WGS-MR prototype has been performed afterwards. The upgrading, by WGS reaction, of a syngas mixture in a membrane reactor integrated downstream a reformer has been proved on pilot scale. The results showed as the integration of the Pd-based membrane tubes allowed up to 20% of hydrogen recovery using only 63 % of the design membrane area. The hydrogen purity grade is of 2.5.

The system, tested for ca. 1000 hours at several operating conditions showed stable performance. During the testing time, an increasing trend of membrane performance has been overall observed. From the initial value, less than 10%, a maximum H2 recovery of 20% has been observed. The increase in WGS feed temperature promoted the H2 permeation.

OCM

The oxidative coupling of methane membrane reactor (OCM-MR) employs MIEC membranes just as the ATR reactor, and just as in such case the use of membranes avoids the use of expensive cryogenic separation for production of oxygen. The match between the temperatures for OCM reaction and permeation of oxygen between 800-900 °C is crucial for this concept. The system holds up to 20 MIEC membranes for oxygen separation.

Following the construction of the OCM prototype in WP6 the factory acceptance tests have been carried out (including HAZOP: Hazard and Operability). The FAT showed leakage from each bundle equipped with membranes. In parallel, a test protocol for the oxidative coupling of methane membrane reactor (OCM-MR) prototype was defined. Due to failure of overall installed membranes, it was not possible to test and validate the OCM-MR prototype.

At the current point in time the DEMCAMER technology applied to the OCM reaction has failed to deliver results beyond the laboratory scale. Significant improvements would have to be made on the robustness of the MIEC membranes before any industrial application under safe conditions could be imagined.

FTS

The pilot scale prototype for Fischer Tropsch in a membrane reactor was build and assembled into a test setup. Two concepts were evaluated in the project: (i) the use of water separation membranes for removal of water from the products which enhances the FTS reaction; (ii) the use of hydrogen permeation membranes for controlled distribution of the H2/CO ratio along the reactor. The pilot scale system used concept (ii) with 5 Pd-based hydrogen permeating membranes.

Following the construction of the FTS small prototype the factory acceptance tests have been carried out (including HAZOP: Hazard and Operability). In parallel, a test protocol for the FTS membrane reactor (FTS-MR) prototype was defined.

The testing of the FTS-MR prototype has been performed afterwards. According to the results the FTSMR prototype cannot be validated to obtain hydrocarbons higher than C5. The mainly products obtained were water, methane and CO2. This means that the reaction had progressed to the production of methane.

At the current point in time the DEMCAMER technology applied to the FTS reaction has failed to deliver results beyond the laboratory scale. The interest of the revised concept of controlled hydrogen addition has not been proven. Significant improvements should be made to validate a pilot scale both the water separation concept as well as the hydrogen distributed feeding concept for FTS.

Figure 19 shows the pilot scale setups for the prototypes in all four industrial processes addressed in DEMCAMER.

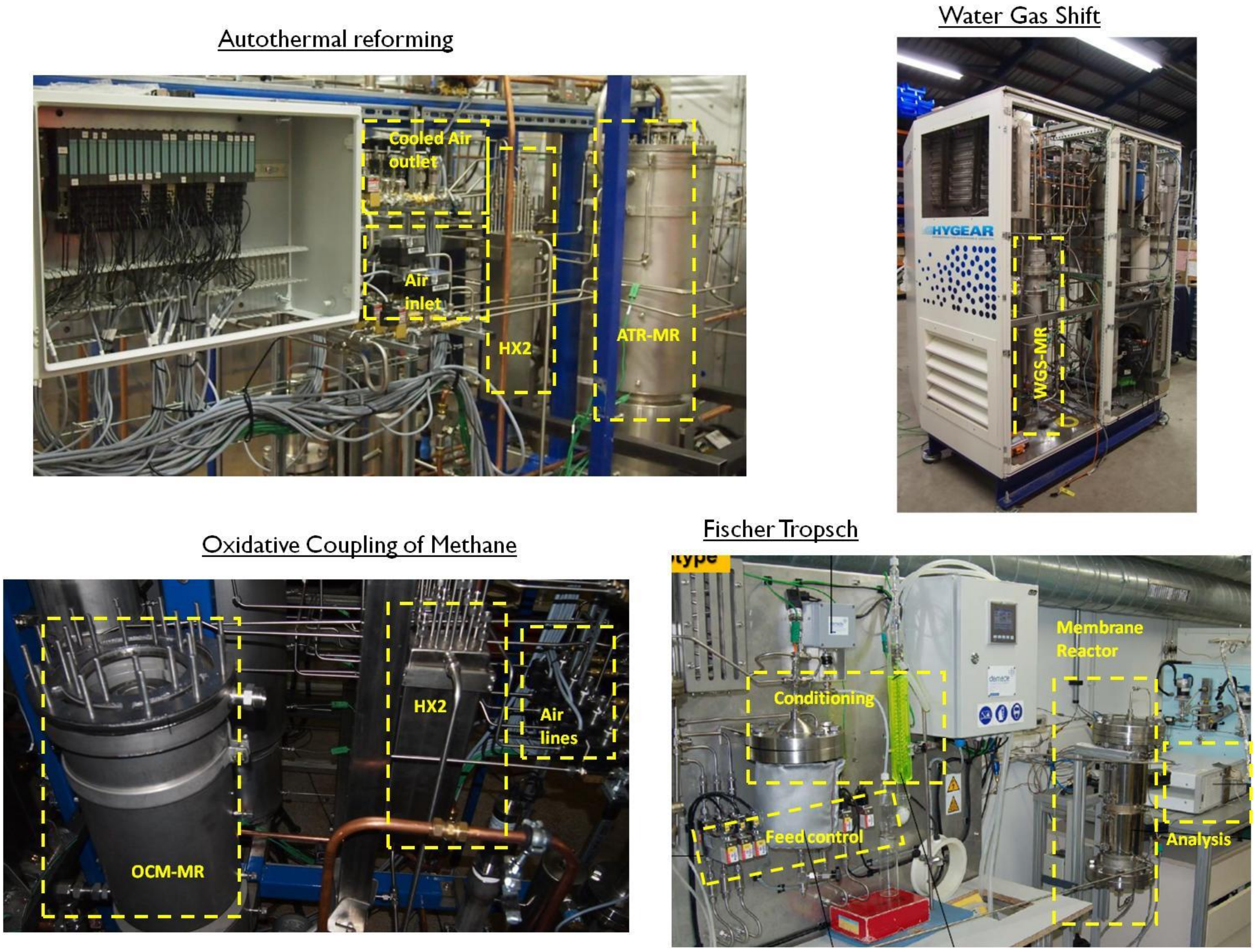

Figure 19. Pilot scale setups for all four processes in DEMCAMER

The systems are controlled with PLC. The level of automation and integration vary from manual operation to complete automation. With the complete automation of the systems a test plan can loaded in the program allowing an automated schedule of tests. Most of the units included SCADA interface which allow the user to fully operate and monitor the system remotely. Figure 20 shows examples of SCADA interfaces used.

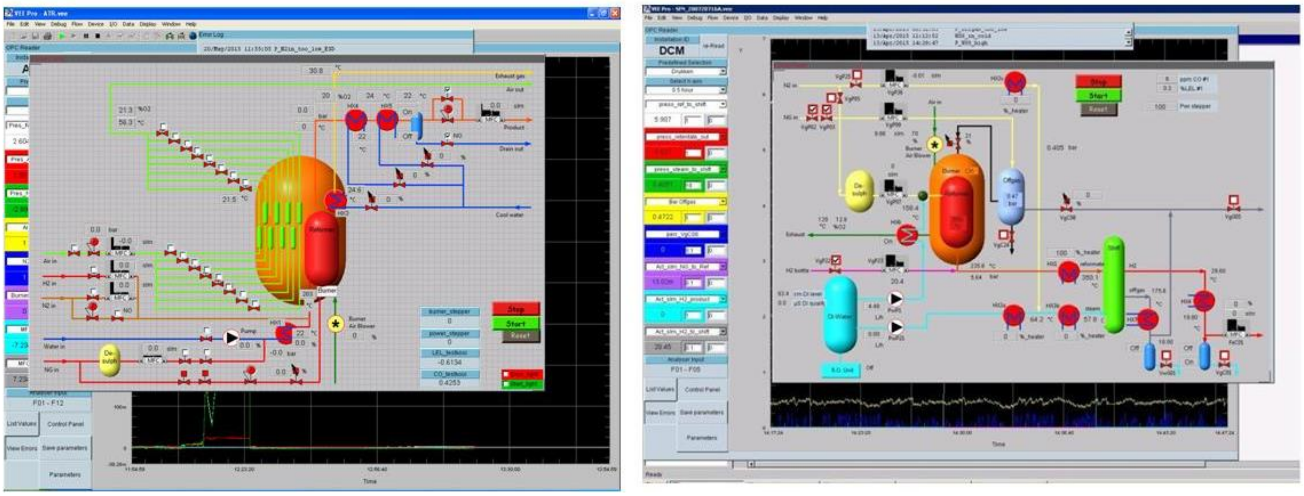

Figure 20. Example of SCADA interface for system control & monitoring

4.1.3.5. Modelling and simulation

The activities modelling and simulation mainly concerned the modelling of the behaviour of membranes and catalysts, the transport in membranes as well as the simulation of catalytic membrane reactors (MR) for the four processes studied in the project: ATR, WGS, OCM, and FTS. Main progress towards objectives and significant results are detailed hereafter.

Ab initio calculation for membranes and catalysts
The aim was to develop an *ab-initio* investigations free from fitting and adjustable parameters for zeolite and metallic membranes, as well as for catalyst particles to be used in WGS, ATR, OCM and FTS.

- A computational procedure allowing the selection of zeolites on the basis of their ideal separation factor in a broad range of temperatures and different initial conditions was developed. It provided good results for analysing and optimizing crystalline nano-porous materials such as heterogeneous FAU zeolites adapt to Water Gas Shift gases purification *via* membrane processes.

- Ab-initio investigation on the H_2 trapping as function of the composition of V-based alloys was carried out in this Task. An atomic cluster approach was used to estimate the most favourable arrangements of the hydrogen atoms in the considered alloys and the H_2 trapping energies. In Figure 21 it is shown two examples: the former refers to a non-equivalent arrangement of hydrogen atoms corresponding to the configuration c^1, while the second refers to an arrangement corresponding to the configurations c^{2o} (both with the biggest distance between H atoms), respectively. The achieved conclusion is in agreement with the experimental result. Thus, this work proposed an *ab-initio computational* method to optimize the composition of metal alloys for increasing the hydrogen permeability.

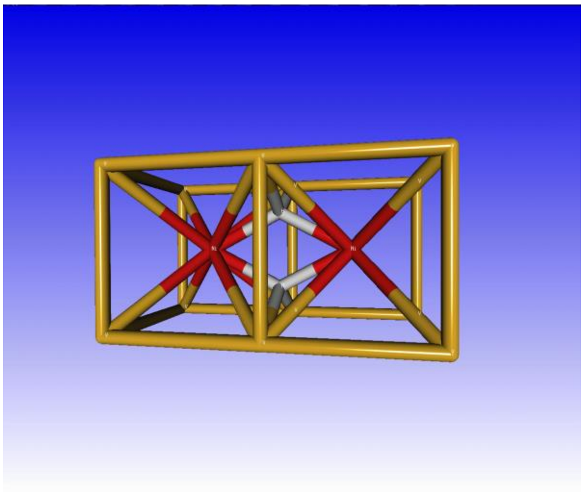

Figure 21-a. Hydrogen non-equivalent arrangements of hydrogen atoms corresponding to the configuration c^1 with the biggest distance between atoms.

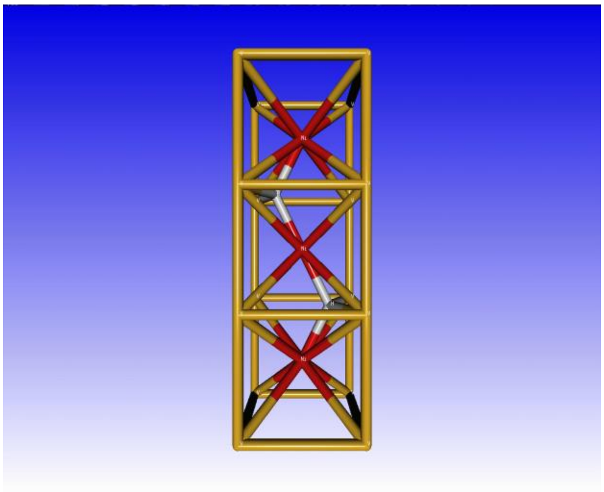

Figure 21-b. Hydrogen non-equivalent arrangements of hydrogen atoms corresponding to the configuration c^{2o} with the biggest distance between atoms.

- Ab initio calculations for the core-shell Ru-Co nanoparticles were carried out with VASP software, chosen for its high computational efficiency and chemical reliability. DFT results pointed to a preferential core-shell formation on the Ru-Co system than in the Ru-Fe. Comparing the pure metals reactivity, the most active towards CO adsorption resulted the Ru (0001) surface that holds the CO molecule in a hole configuration, favouring its dissociation mechanism as a starting point of the FTS. Energetic and structural parameters results for the bimetallic surfaces were estimated. As an example, the optimized structures obtained for the Ru-Co system are displayed in Figure 22.

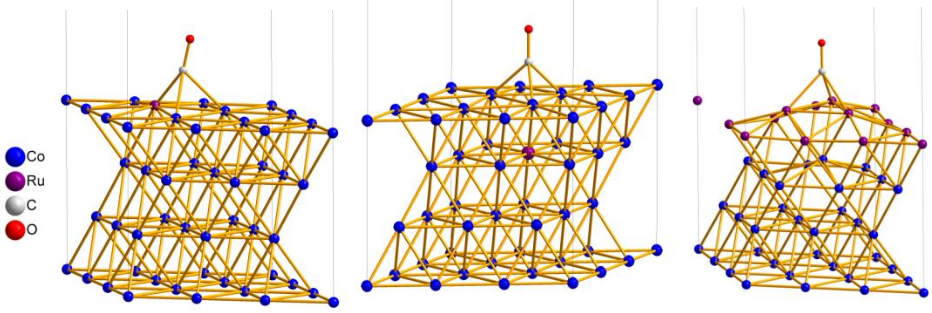

Figure 22. CO adsorption over Ru-Co bimetallic surfaces: a) Rutop/Co(0001) b) Rusub/Co(0001) c) Co(0001) @ Ru core-shell.

- The possible structures of selected catalysts for ATR by using a combination of DFT and Hartree-Fock were identified. With the use of cluster approach model CeO_2 oxide particles along with CeO2-supported Ni4 and Ni6 clusters were investigated at the B3LYP level of DFT. The obtained results for Ni clusters on ceria imply strong interaction of metal particle with the oxide support resulting in (1) electron transfer from metal particle to oxide, (2) penetration of nickel into "bulk" of oxide, (3) reduction of the cerium centers by metal via the interface oxygen layer and formation of nickel oxide motif. When introduced in nickel cluster the carbon atoms decompose metal particle to form carbide-like structures. An example of cluster models for CeO_2 at the B3LYP level using the 6-31G* basis set for oxygen and the CEP-31G is reported in Figure 23 and Stuttgart/Dresden pseudopotential for Ce (Gaussian09 package) in Figure 24.

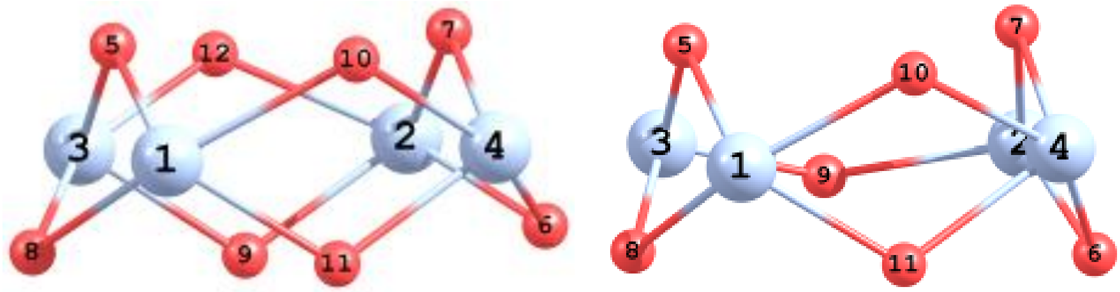

Figure 23. The Ce_4O_8 cluster ($\langle S^2 \rangle$=4.100) and oxygen-vacancy-containing cluster Ce_4O_7 ($\langle S^2 \rangle$=3.095) optimized at the B3LYP/6-31G*(oxygen)/CEP-31G(Ce) level (Gaussian09)

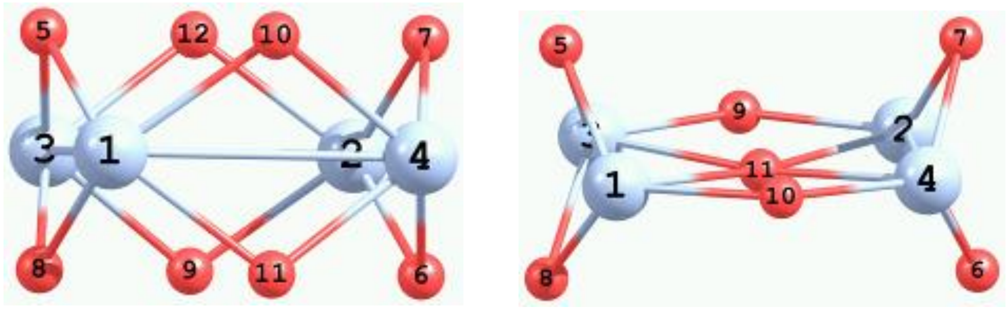

Figure 24. The Ce_4O_8 cluster ($\langle S^2 \rangle$=0.000) and oxygen-vacancy-containing cluster Ce_4O_7 ($\langle S^2 \rangle$=1.003) optimized at the B3LYP/6-311G(d,p)(oxygen)/ Stuttgart/Dresden ECP (Ce) level (Gaussian09).

- Ab-initio calculations were used to clarify the mechanism of OCM by tungsten center at silica possible structures of such center by building a cluster model of the α-cristobalite (111) surface. All calculations were performed at the B3LYP level using the LANL2TZ(F) and 6-311G** basis sets for tungsten and lighter atoms, respectively. Based on this result one may guess that the true OCM active center is that associated with Mn(+5) complex having terminal oxygen ligand with a radical character. In Figure 25 the OCM process is modeled for heterolytic cleavage of the “first” C-H bond.

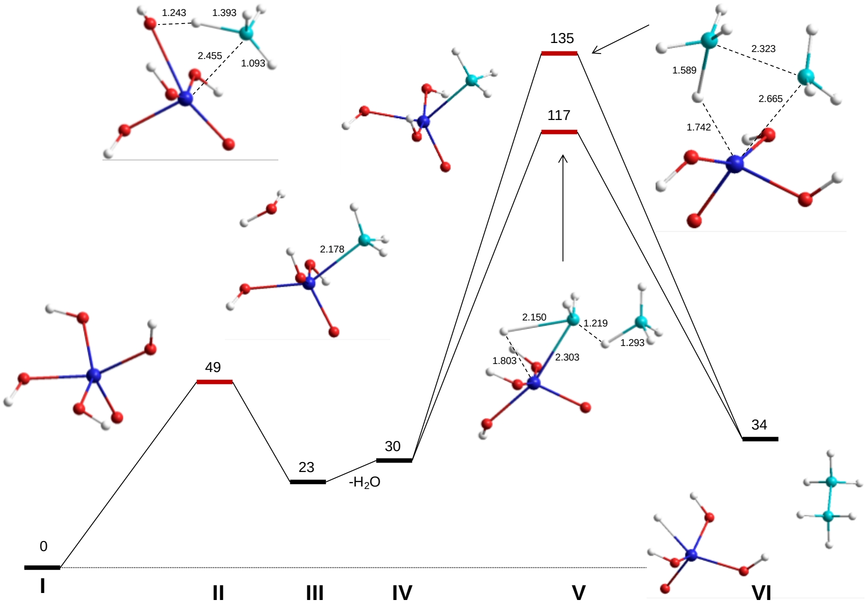

Figure 25. Heterolytic route for OCM with $WO(OH)_4$.

Transport in membranes

The transport of gases through the various types of membranes developed in the project was also analysed:

- The transport in the MIEC membranes was modelled by a set of equations selected on the basis of the experimental permeation results obtained as a function of temperature and sweep gas flow rate. The expression for the description of the permeation through the membrane is available and the parameters for different membranes were determined. This expression (based on Xu’Thompson’s model) was used in the modelling of ATR and OCM.

- Hydrogen transport in the Pd-based supported membranes was modelled identifying the elementary steps of the permeation process. It allowed evaluating the hydrogen profiles along the membrane layers and in the gas phase layers adjacent to the supported membrane and to calculate quantitatively the influence of each step on the whole permeation process. The effects of both concentration gradient/polarization and inhibition on hydrogen permeation were correctly evaluated and used for MR simulation performance (Figure 26). The simulation results showed also to what extent these phenomena could affect the performance of the Water-Gas Shift reactor, thus providing useful information for prototype developed pilot-scale.

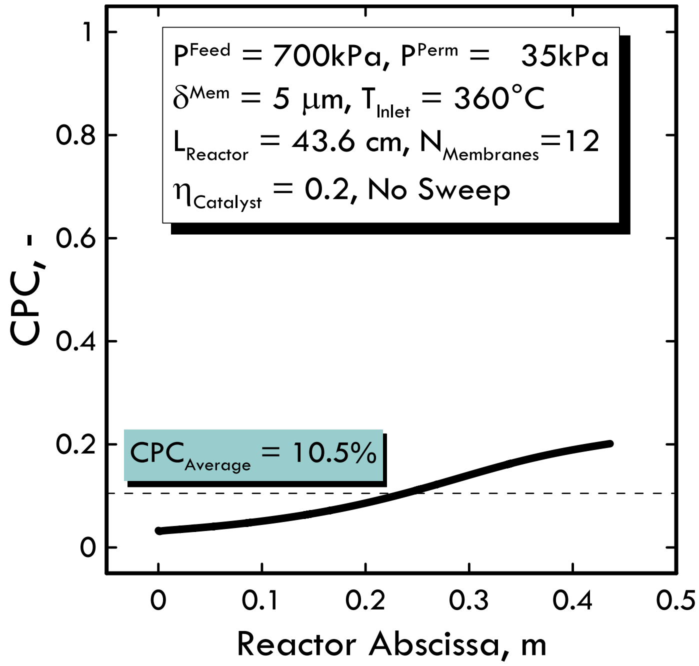

Figure 26. CPC profile in packed bed MR for WGS reaction.

- The transport of light gases like H_2, CH_4, CO_2 and N_2 in zeolites membranes was investigated with a Maxwell-Stefan multicomponent approach, coupled to the Knudsen mechanism when required. The modelling and simulation analysis of the mass transport of multicomponent vapour/gas mixtures through defected zeolite layers was performed for different geometrics and operating conditions, among which a particular importance was paid to the influence of defect degree and defect size (i.e., defect mean pore diameter). The selectivity moderately decreases with increasing feed pressure and water vapour content and dramatically decreases with increasing defect size and degree were the main results. Therefore, just a small increment of defects over the zeolite surface determines a strong drop of the membrane performances in terms of separation factors owing to the presence of zones in which surface diffusion is replaced by the Knudsen mechanism and viscous flow. This analysis was of specific interest in FTS modelling and simulation, confirming the necessity of defect free zeolite membranes for this making attractive the FTS in an MR.

Simulation of the CMRs

The membrane reactors were simulated for the four processes of interest aiming to analyse their performance as function of the various operating parameters and the various configuration of the reactor.

- Methane partial oxidation reaction system at high GHSV for a LaCrRuO3 catalyst developed in WP3 was investigated in Fluidized bed MR. The kinetics of the new catalyst was studied and incorporated in the ATR model. The reactor was modelled and a sensitivity analysis was also carried out. The model was used to refine the ASPEN calculations.

- WGS reaction was investigated in fluidized bed MR and packed bed MR. In the first case, a typical 1D two-phase phenomenological model was developed and used for description of the experimental data of permeation and reaction at lab scale and for the design of the reactor for the pilot (Figure 27).

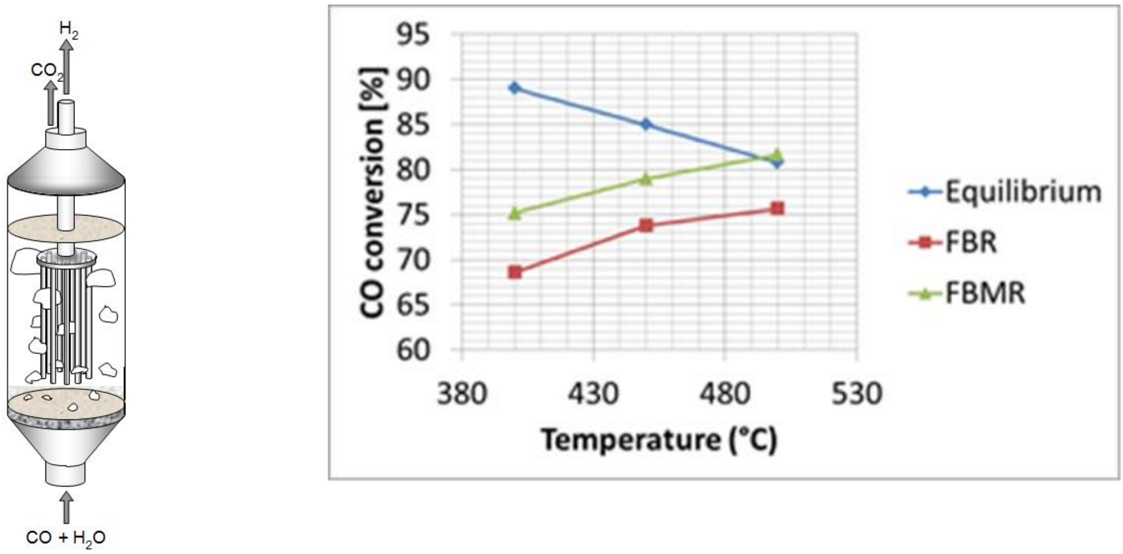

Figure 27. Fluidized bed MR scheme and CO conversion as function of temperature.

- The model for the simulation of the performance of a fixed bed MR was integrated with the information on the rate determining steps of the permeations as described in WP8.2 and was used to analyse the performance of an MR for WGS reaction equipped of a Pd-based membrane having the characteristics of the membranes developed in the framework of WP4. The model took into account the concentration polarization phenomena occurring during reaction (Figure 28). After comparison with experimental results at lab scale it was used for the design of the packed bed MR at pilot scale.

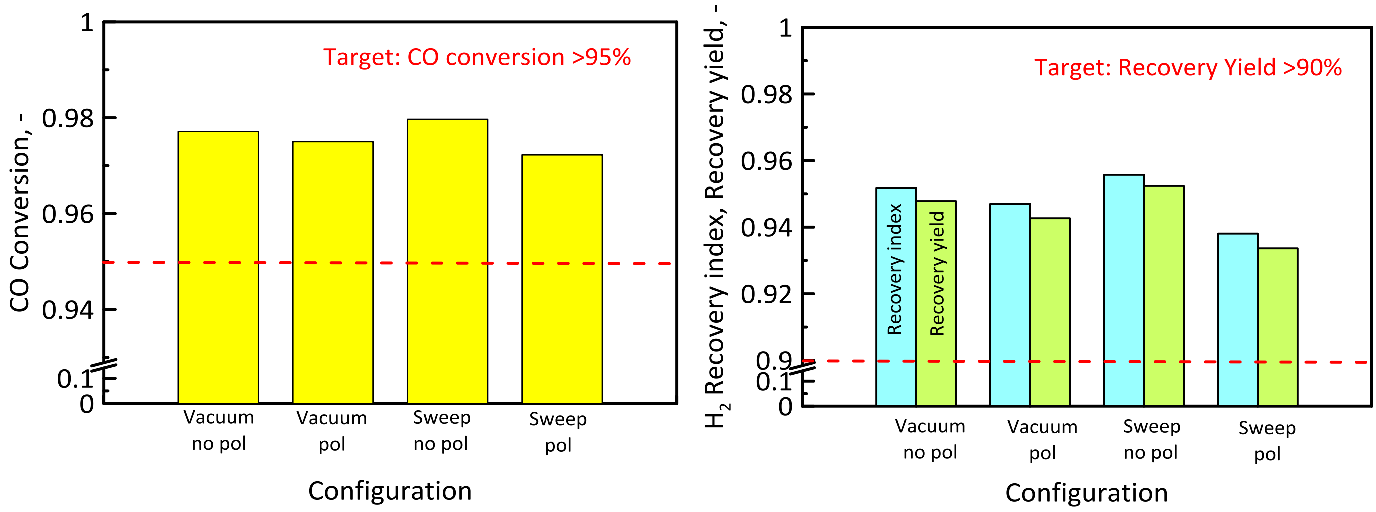

Figure 28. CO conversion, hydrogen recovery and yield for the vacuum and sweep configuration.

- 1D numerical simulation model was defined to study and better understanding the OCM reaction in MIEC-MRs. The reactor was simulated and the results compared with different reactor configurations (Figure 29). The distributive feeding shows superior performances in terms of selectivity and yields compared with other reactor types. Additionally the air separation (which is a major cost in OCM plants) is integrated in the reactor achieving a double beneficial effect of the final economic performance of the reactor/system. This model was used for the MR design at pilot scale.

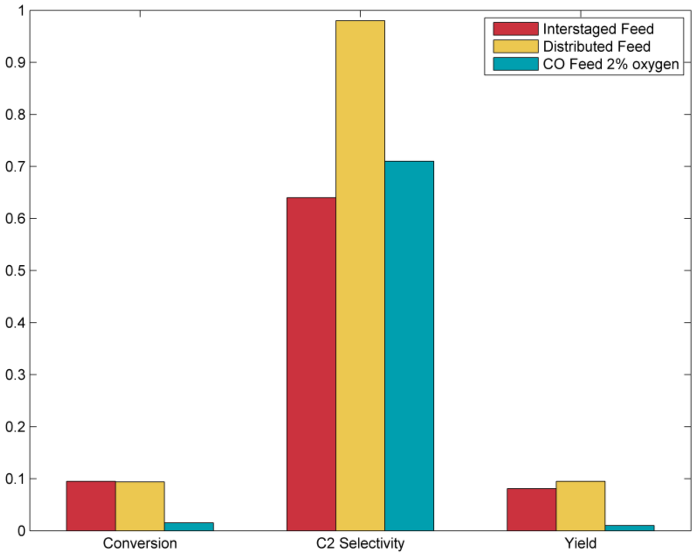

Figure 29. Comparison of the three feed modes are shown above. The y-axis displays the fraction of the total. The x-axis displays the three results which have been compared.

- 1D numerical simulation model to study the FTS catalytic MR was defined and validated for porous membranes, after incorporating the kinetics for the FTS catalysts obtained experimentally. Only the H2 feed concept was simulated so far because is the only concept that was proven at lab scale. This model was used for the MR design at pilot scale.

Process design and simulation

The simulations of the transport of membranes and lab-scale CMR were used as input in the design and simulation of the four processes of interest.

- A 1D model was coupled with ASPEN to evaluate the effect of the reactor size and design on the ATR process efficiency (Figure 30).

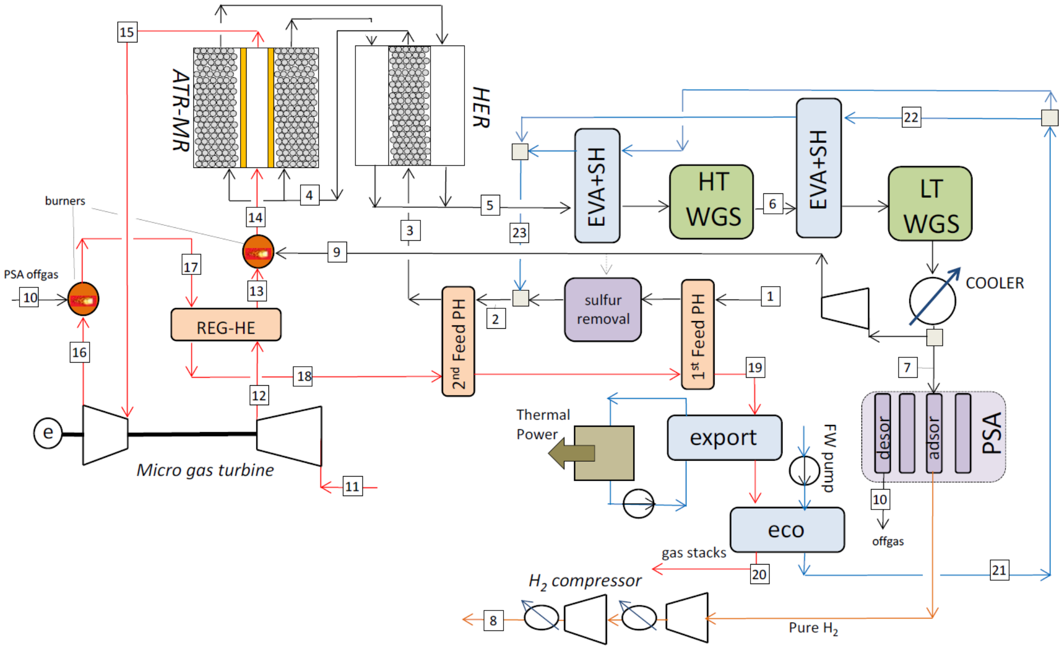

Figure 30. Plant design for the ATR system.

The results show that the reforming efficiency is approaching 70% (the equivalent reforming efficiency is about 76-77%) which is slightly lower than the system operated with fired tubular reforming as presented in (Martínez et al., 2013). However, this configuration was designed for small-medium scale applications and therefore the operating conditions, such as the steam production and the turbomachines are not as efficient as in the case of large scale H2 plant. The combination of the ATR-MR with HER allows recovering efficiently the heat of the syngas and reducing the heat duty for the reforming; however the cost of the entire system must be verified.

- A new process integrated with WGS-MR was designed where H_2 separation and purification (PSA) is no longer required since more than 90% of H_2 produced is directly recovered in the permeate stream with a purity of 99.99% (Figure 31). Two scenarios were investigated; they being vacuum or sweep gas on permeate. In both cases the effect of concentration gradients on the packed bed MR performance was taken into account. The hydrogen production and CO conversion of both configurations exceeded the targets set in the specifications. The “vacuum” configuration resulted the most promising in terms of both CO conversion and hydrogen recovery; therefore, it was selected by HYGEAR to implement the simulations of the pilot. Various options for retentate post processing were investigated all resulting in a reduction of the extra natural gas required by the burner. Overall, the integrated system showed positive assets in terms of CO conversion and pure hydrogen production as well as of raw material exploitation and energy consumption.

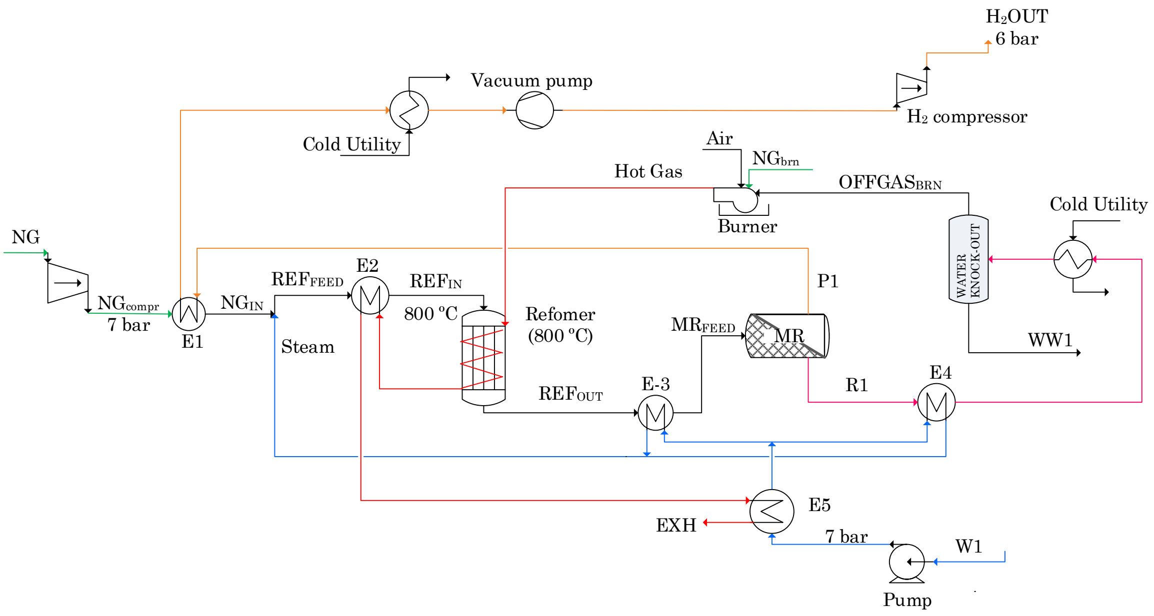

Figure 31. Process flow diagram for vacuum configuration including heat exchangers network.

- A new process FTS carried out in an MR. The results show that the best conditions for operating the FTS-MR system with the Ru-B/TiO_2 catalyst are 280ºC, 10 bar, H_2/CO =2 and 7.500 mL(H_2+CO)/gcat·h. The results obtained in the tests show that the use of packed bed MR for the H_2 distributed feeding concept results in an increase of both the selectivity and CO conversion (Figure 32). With respect to the economic evaluation of the system, the minimum selling price of FTS diesel obtaining with the DEMCAMER technology was calculated and compared to conventional technologies prices. The simulation process had been done according to lab data, which means that in order to carry out scaling up; a big effort has to be done. This scaling-up effort had not been considered in the economic evaluation. The minimum selling price obtaining for the diesel was 0.9 €/L, similar price to the price of biodiesel.

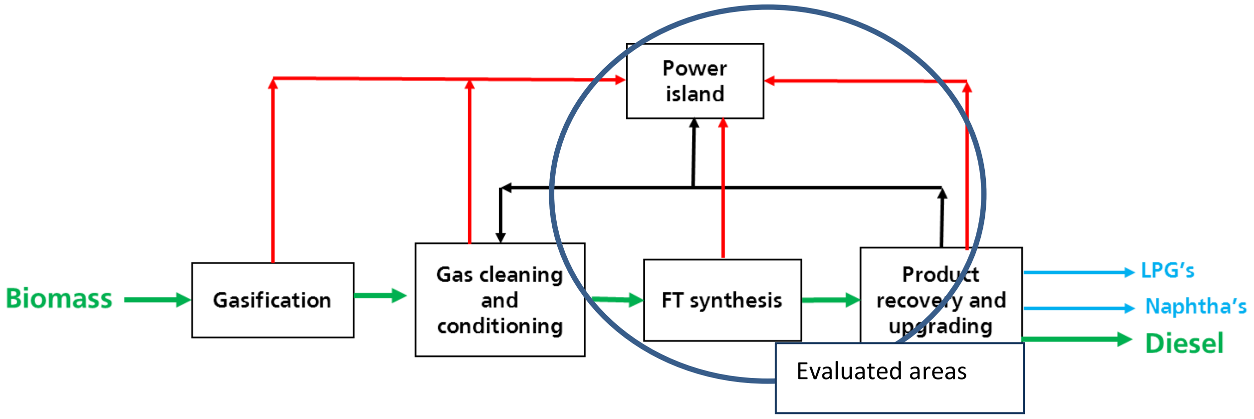

Figure 32. Evaluated areas in the FTS process.

- The plant performance reflecting the effect of using MR technology for the OCM process was investigated. The model was used to size some of the subcomponents, to aid the optimisation of the system and to help the explanation the measurements when the reactor is tested. A parameter study was performed with the optimized output set for C_2 production and yield. Results show that the optimal operating conditions are at 870°C and O_2/C feed ratio ~ 0.3. The model and optimization was also useful for the definition of the test plan in WP7.

Pilot scale modelling

Pilot scale models of the processes were extended from the preliminary version. When having results from pilot scale tests it was possible to validate and improve the models.

Control strategies for the pilot systems were developed. The first phase of the control definitions was through specification of Input/Output control and monitoring variables. The final definitions of the control strategies were expanded with the control logics as implemented in the PLCs. The ATR, OCM and WGS systems used local control with PLC and remote SCADA interface. The controls allow the systems to perform a predefined set of testing conditions following a test plan without the need of an operator. The FTS system used manual controls owing to the contained scale of the unit and reduced duration of the test plan.

4.1.3.6. LCA and safety issues

Comparison of CMR technologies to reference technologies from a life-cycle, safety and socio-economic perspective was performed. The socio-economic analysis focused more specifically on three configurations of hydrogen production, i.e. ATR process and WGS at large scale and small scale, in comparison with reference cases. The socio-economic analysis includes traditional economic indicators that aggregated monetary and non-monetary values on investment indicators. Based on time series analysis, main inputs included market prices such as natural gas, electricity, labour, water, catalysts and membranes were forecasted. As a result, an operational net present value (NPV) was estimated for each of the CMR and reference configurations. The socio-economic analysis integrated also 'non-monetary costs and benefits' and focused on environmental and health issues, including the LCA results. An "environmental net present value" (*En-NPV)* was then estimated for the different configurations. A sensitivity analysis has been performed. It concentrated on three aspects: the impact of a decrease of electricity price, the variation of carbon price assumptions – which is a sensitive parameter with regard to the *En-NPV* – and the extension of the CMR membrane lifespan from 1 year to 2 years and to 5 years – which impacted significantly the operational cash flow and the profitability in all configurations.
The following points can be outlined from the various assessments:

- In the case of the ATR process, the CMR process represented lower environmental impacts compared to reference technology for water withdrawal, due to the lower amount of steam needed, but appear less interesting for GHG emissions, due to a higher amount of natural gas feedstock, and higher electricity consumption. The impact of infrastructures on human health is also higher for the CMR technologies, due to the use of palladium for the catalyst. From a safety point of view, CMR and reference do not present significantly different risk levels, although toxicity hazard potential was higher for CMR technology in case of leaks located at the outlet of the reactor. However, it can be stated that a future CMR process with CO-shift in one step and no assistance of the ATR reactor with a burner, may be slightly safer than SMR process, provided that issues related to the current weak membranes are solved. With regards to socio-economic aspects, net present value (NPV) - configurations studied with membrane lifespan of 1 and 2 years and configurations based on an ATR process had lower NPV than, the reference case. Considering the environmental net present value (Env-NPV) - configurations studied with membrane lifespan of 1 and 2 years and configurations based on an ATR process have lower Env-NPV than the reference case. In the context of a low CO2 price assumption, performances of these two configurations can be considered as comparable.

- For the WGS, a small scale and a large scale process were considered.
  - At large scale, the CMR technologies showed an interesting alternative for the GHG emissions, and for the impact on resources depletion. However, since the electricity consumption is higher for both CMR technologies, the water withdrawal, the impact on human health and the impact on ecosystem quality remain lower for the conventional WGS large scale technology. In addition to the higher electricity consumption of the CMR technologies, the infrastructures represent higher impact on human health due to the use of Palladium for the membranes. The large scale WGS CMR configuration with a membrane lifespan of 5 years showed a higher NPV than reference configuration. The Env-NPV of the large scale WGS CMR configuration with a membrane lifespan of 5 years is lower than the one calculated for the reference case. In the context of a low CO_2 price assumption, performances of these two configurations can be considered as comparable.
  - At small scale, the CMR technology represented equivalent or slightly higher impacts on climate change and on resource depletion, but as for the WGS large scale, the CMR technology showed much higher water withdrawal, impact on human health and impact on ecosystem quality. In fact, while the amount of natural gas consumed and the amount of steam is lower for the CMR technology, the electricity needed for the process is much higher than for the conventional technology. As far as the large scale technology is concerned, the infrastructures represented higher impact on human health due to the use of palladium for the membranes. The operational cost of the CMR technology does not compensate environmental costs. The comparison highlights the need of potential improvements for a membrane lifespan of 5 years.

  Among configurations studied, the large scale system showed better socio-economic performance than the smaller ones (269 tonnes/year natural gas input instead of systems with an input within a range of 16-20 tonnes/year). Also, the importance of membrane lifespan for the overall performance of processes using CMR was underlined. The safety benefits were significant for CMR WGS technology compared to traditional WGS configuration, mainly because of the removal of hydrogen from the main stream. At both small and large scales, CMR WGS configurations are safer than the traditional WGS reference process.

- The only processes for which the CMR solution represents lower impacts for all the environmental indicators are the OCM process (for which the yield of the processes is exactly the same but with lower electricity and compressed air consumption) and the FTS process, showed a higher yield and higher selectivity of heavy hydrocarbons than the reference process. From a safety perspective, the OCM was compared to methanol-to-olefin process as no conventional OCM exists and it appeared that conventional process was safer than CMR technology. However, the MTO process is much more mature than OCM prototypes. For FTS process, the CMR technology presented a higher thermal runaway risk at large scale compared to reference technology. However, consequences of hazardous events look lower for CMR than reference, mainly because CMR technology operates at much lower pressure compared to its corresponding reference technology.

The results on the CMR technologies showed mixed trends compared to conventional technologies. The results could be better, worst or comparable from a sustainable point of view depending on the indicator considered (global perspective taking into account socio-economic aspects, safety and life cycle assessment). The conclusions that were drawn needed to take into account the following points:

- Work performed showed that there are various important aspects to be considered when comparing systems. First of all, the amount of feedstock is a crucial parameter to decrease the impacts of the process, in particular for the GHG emissions and the impact on resources depletion. However, it is necessary to also consider the heat and electricity consumption needed for the process, since an increase of one of those two parameters could offset the impact reduction obtained from a reduction of feedstock amount, and even reverse the conclusions. The electricity consumption is also one of the main contributors to the total water withdrawal, together with the steam consumption. Finally, a last parameter to be taken into account is the use of palladium for the infrastructures (catalyst and membrane), since it represents a large contributor to the impact on human health.
- The actual safety level of the final plants will of course depend on the implemented safety barriers. If efficient and reliable solutions can be implemented to immediately stop the flow in case of ruptured membranes (e.g. specific system developed by Hygear partner) and that membrane mechanical resistance is improved, provided that the CMR configuration does not create potential runaway concern at large scale, the overall safety level of the new CMR reactors should be either similar to the conventional technologies or even better compared to reference processes.
- Concerning the SEA, a number of recommendations for future improvements of CMR hydrogen production units were provided:
    - Decarbonisation and overall environmental improvement by electricity: electricity consumption is a critical trigger for process improvement; it is noted electricity consumption is a key parameter in the variation of the DEMCAMER environmental net present value. A decrease of electricity consumption would significantly decrease the operating costs and – under the hypothesis of the actual energy mix in Europe – decrease significantly environmental impacts through decrease of climate change and air quality impacts.
    - Taking into account climate change impacts: for the small scale ATR (CMR) case and the large scale WGS (CMR) case the inclusion of a carbon capture system may significantly improve the environmental impact of the technology and then, the social benefit of the technology – compared to reference technology;

Depending upon the scenarios and considered factors, the CMR technologies may be more interesting in some aspects and less in others compared to the reference technologies. The provided elements will help stakeholders to guide potential future deployment of CMR technologies by taking into account the deployment perspectives, the corrective measures and by being risk-informed.

4.1.4. Potential impact

Traditionally, Europe has been dominant in chemicals production, a position which has weakened in the past few years. Recognising the industry's strategic importance, China and India have made successful efforts to build up large and increasingly sophisticated production facilities.

According to the European Chemical Industry Council (CEFIC), in 2012, with 556.6 billion € sales, the EU chemical industry has lost its first place in the ranking to Asia (1726 € billion), mainly due to the rise of China and India. This represents a decline in global market share from 30.5% in 2002 (€290 million) to 17.8% in 2012. Consequently, the EU's share of global chemicals production is decreasing in several segments. Europe's competitive position is at risk for his lack in competitiveness. The research and implementation of Process Intensification, such as catalytic membrane reactors, can help to increase the competitiveness of the EU Chemical Industry.

It is well understood that the reactor is the heart of any chemical process (which also influence size and costs of downstream separation processes), and therefore most of the chemical industry would benefit from the implementation of membrane reactors in their processes, integrating reaction and separation steps in one unit, reducing the energy costs and the environmental impact (lower by-products). An EU study indicates that the potential energy saving across the chemical sector using "Intensified Reactors" is about 11 PJ/year[i]. These benefits could also be extended to other sectors, including glass and metals[ii]. On the other hand, by the integration of Reaction and Separation into one step will reduce the needs of materials down to a 40% compared to standard processes[iii].

Hydrogen production

Hydrogen has been mainly used in the last 100 years as chemical product for different industrial applications (ammonia synthesis, methanol production, petroleum refining, etc.), with an annual production of about 55 million tons, increasing by approximately 6% per year. It is important to underline that most of the produced hydrogen (about 85%) is consumed where generated, while the remaining 15% is commercialized.

Almost a 50% of the global production for hydrogen is currently generated via steam methane reforming, therefore coming from natural gas with a 70-80% efficiency. About 30% of the hydrogen produced comes from oil/naphtha reforming from refinery/chemical industrial off-gases, 18% from coal gasification, 3.9% from water electrolysis and only a 0.1% from other sources. The different shares of the global hydrogen production and consumption are reported in Figure 33. Therefore, above 95-97% of hydrogen today is produced from fossil fuels using high-temperature chemical reactions that convert hydrocarbons to a synthetic gas, which is then processed to make hydrogen. The conversion of natural gas into hydrogen takes place in catalytic reactors (reformers), in centralized locations with a typical hydrogen production rate of more than 10.000 Nm^3/h. In this way of supplying hydrogen to the customers, two thirds of the energy content of hydrogen produced is wasted as compression energy and the required transportation energy. On-site hydrogen generation systems are intended to overcome these drawbacks (see Figure 34).

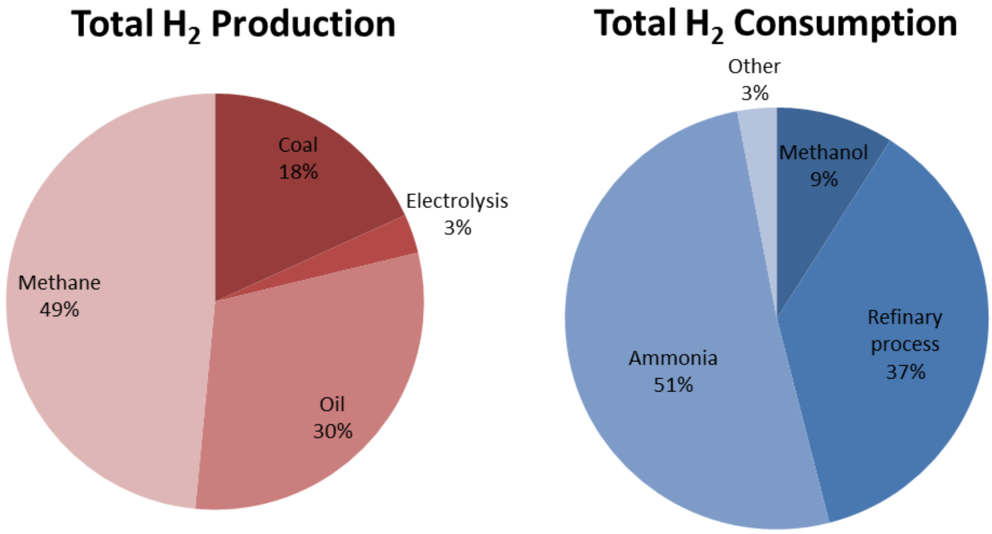

Figure 33.Total hydrogen production and consumption

Figure 34. HyGear's (HT&S) on-site hydrogen generation systems: Left: 5 Nm3/h system ; Right: 50 and 100 Nm3/h system

One promising new concept proposed in DEMCAMER is the hydrogen membrane reformer, which combines the advantages of the reforming reaction with the separation of hydrogen. The DEMCAMER is basically a membrane-assisted reformer that circumvents the equilibrium limitations of traditional systems by selective removal of hydrogen. As such it allows higher yields at much lower temperatures than conventional systems and thus it reduces energy requirement practically to the theoretical minimum while also resulting in cost savings. Furthermore, this approach is directly answering to the increasing industrial demand in hydrogen (fertilizer industry, food processing, semiconductor industry, glass manufacturing, metal treatment, etc.), at pressure ranges of less than 10 bar with continuous hydrogen flows between 5 Nm^3/h and 250 Nm^3/h.

Another aspect of on-site hydrogen production is supporting the development of a hydrogen infrastructure and thus the transition of hydrogen into the market [[iv]]. A hydrogen infrastructure is required for the refilling of hydrogen-propelled vehicles as cars (both internal combustion and fuel cells), busses and fuel cell driven bicycles. The hydrogen produced by the on-site hydrogen generation systems is offered in the required hydrogen quality for the production process and at required product pressure (less than 10 bar).

Estimated Compound Annual Growth Rate per Application Sector	
H_2 production. Hydrogen has a variety of applications ranging from petroleum recovery and refining to chemical and fertilizer production, metal production and fabrication, food processing, electronics, fuel cells, pharmaceutical, aerospace, glass production, welding, and R&D labs, among others. The hydrogen generation market will grow from an estimated €97.5 billion in 2014 to €130,2 billion by 2019, with a CAGR of 5.9%[v].	**5.9 %**

Liquid Hydrocarbons production

Currently, the largest part of our energy used (electric power generation, heating, and transportation) is based on fossil fuels. In the last decade alternative and renewable energy resources became increasingly important for several reasons, mainly to combat greenhouse emissions, but also to ensure security of supply and a lower increase of costs for energy by reducing fuel import dependency. Sustainability in energy supplies may require new concepts with respect to feedstock, production and the final products. Improvements in overall efficiency of the technical process are necessary as these will directly lead to lower emissions of CO_2, besides NO_x and unburned hydrocarbons, thus contributing to a more environmental friendly energy production.

For the transport sector, several activities are ongoing leading to the operation of cars and trucks with natural or biogas, ethanol or biodiesel and to the development of fuel flexible and hybrid cars. A key for the success of these concepts is the availability of certified fuels to convince the consumer of buying these products, as to be seen in the introduction of E5 in Europe and E10 to gasoline in Germany. The road transportation sector is also becoming part of the efforts finding alternatives to fuels from fossil sources. The gasoline and diesel from crude-oil have been the only road fuel worldwide available since decades. The total consumption of transport fuel is about 30.4 million barrels per day [vi,vii].

Today, road fuels constitute about 55.5 percent of the global oil consumption and they are responsible for about 25% of the overall CO_2 emissions worlwide [viii]. Besides, global population is growing and demand for mobility is increasing and a further increase of the road traffic is foreseen. The number of vehicles on the road is expected to double to more than two billion by 2050[ix]. If fuel consumption and hence CO_2 emissions will continue to grow at the same rate, in 2050, the CO_2 emissions would be almost 5 times higher than today.

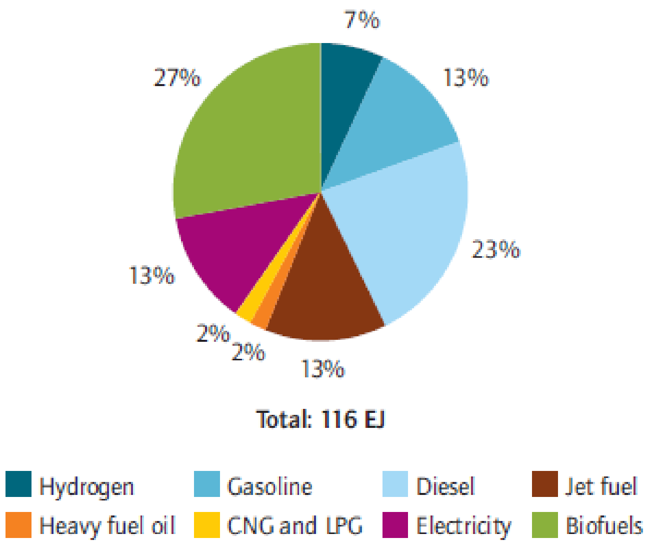

Figure 35. Global energy use in the transport sector.

Substitution of oil therefore needs to start as soon as possible and increase rapidly to compensate for declining oil production, expected to reach a peak within this decade. Climate protection and security of energy supply therefore both lead to the requirement of building up an oil-free and largely CO_2-free energy supply to transport on the time horizon of 2050. The current energy policy agreed by the European Commision included a renewable energy roadmap proposing, among other measures, a binding 20% target for the overall share of renewable energy by 2020.

Decarbonising transport is a core theme of the EU 2020 strategy[x] and of the common transport policy. The long-term perspective for transport in Europe has been laid out in the Commission Communication on the Future of Transport of 2009[xi]. The long-term objective of the European Union on CO_2 emissions is an overall reduction of 80-95% by 2050. Production costs of biofuels vary widely across processes and geographical regions. The main differences in biofuel production costs are due to feedstock prices, the process energy used, and the prices received for by-products from the production process. Thus costs can be highly variable dependent on the various combinations used in each country. Cost estimates for 2nd-generation biofuels show significant differences depending on plant complexity and biomass conversion efficiency. Important factors include annual full-load hours of plant operation, feedstock costs and capital requirements. Accordingly, biofuel plants with a higher biomass-to-biofuel production ratio are typically able to accept higher biomass supply costs compared to less efficient plants. IEA confirms that the overall costs for synthetic fuel production from biomass (BtL technology) were about 1 €/L in 2010, with projected a reduction of 10-15% in these costs by 2015 and 20% by 2030[xii] (see Table 5).

Table 5. Production cost (USD/litre gasoline equivalent).

	2010	2015	2030	2050
Petroleum gasoline	0.54	0.72	0.82	0.83
Ethanol - conventional	0.70 - 0.75	0.70 - 0.80	0.65 - 0.85	0.65 - 0.85
Ethanol - cane	0.60 - 0.70	0.60 - 0.70	0.60 - 0.70	0.60 - 0.70
Ethanol - cellulosic	1.05 - 1.15	0.90 - 1.05	0.80 - 0.95	0.80 - 0.90
Biodiesel - conventional	0.95 - 1.05	0.95 - 1.10	0.95 - 1.15	0.95 - 1.15
Biodiesel - advanced (BtL)	1.05 - 1.15	0.90 - 1.05	0.80 - 1.00	0.75 - 0.90
bio-synthetic gas	0.90 - 1.05	0.85 - 0.95	0.75 - 0.90	0.70 - 0.85

Note: Costs reflect global averages. Ranges result from the strength of correlation between oil price and feedstock costs and capital costs

Conventional GTL technology utilized by Shell and Sasol is only economic for plants producing 30,000 barrels per day or more. There are only five of these plants in the world, 3 operated by Shell and 2 by Sasol and only about 6% of the world's known gas fields are large enough to sustain GTL plants of that size. In contrast, smaller scale GTL plants are designed to be economic at 1,500 b/d to 15,000 b/d, requiring only 15,000-150,000 million BTUs of gas per day as feedstock. Distributed GTL could unlock up to 50% of the remaining fields that conventional GTL cannot economically exploit. Shell recently announced the cancellation[xiii] of their 140,000 b/d Gulf Coast GTL project due to cost considerations and market uncertainty over the long-term spread between gas and diesel prices. Shell's plant would not have come online until the mid-2020's which highlights the challenges in investing billions in a facility whose business model is based on arbitraging the long-term spread between gas and petroleum prices that are notoriously hard to predict.

The EIA estimates[xiv] very challenging economic prospects for large-scale GTL projects. According to the EIA, GTL plants are more economic when configured to sell waxes and lubricating products because the chemicals market is much smaller than the fuel market. F-T waxes are used to produce candles, paints, coatings, resins, plastic, synthetic rubber, tires and other products. The EIA's analysis suggests GTL developers should maximize wax production.

The membrane Fischer-Tropsch reactor addressed in DEMCAMER project could allow deployment to practically any region of the globe to make use of market gas reserves. Membrane based Fischer-Tropsch process focuses on the production routes of liquid fuels (Gas to Liquid, GTL) from Fischer-Tropsch synthesis (FTS) which is an ideal alternative to existing FTS process, which maximizes the gasoline output, minimizing the obtained paraffinic waxes and increasing the overall process efficiency.
The technology targeted in DEMCAMER project allows processing the mentioned Energy sources helping to reduce the environmental impact of gas flaring and municipal solid wastes and biomass wastes accumulation, producing motor fuels and energy efficiently (syngas could be derived from dry, steam, partial oxidation and autothermal reforming processes using natural gas, coal or biomass). The membrane FTS prototype in the DEMCAMER was targeting to improve the current state of the art F-T reactors by increasing the conversion achieved in the reactor, by suppressing the overreaction and by increasing the gas-liquid interface.

Ethylene production

Ethylene, the simplest of olefins, is by far the most important raw material in the petrochemical industry. Direct applications include, among others, the three polyethylene plastics HDPE, LLDPE, and LDPE as well as petrochemical intermediates, which are in turn mainly used for the production of plastics. Other syntheses lead to the production of solvents, cosmetics, pneumatics, paints, packaging, etc. (Figure 36). Global ethylene production capacity on January of 2013 was over 143 million tonnes per year (Mtpy) and is predicted to be growing with the annual rate of 3% until 2020. Detailed information about the recorded and predicted trends of ethylene production worldwide is available in several reports and reviews which suggest a dynamic and distributed market of this product all around the world. As shown in Table 6, around 30% of the total ethylene production is delivered by Asia-pacific region and the rest is produced mainly in North America, West Europe and Middle East.

Table 6. Worldwide ethylene production by region* and feedstock.**

Region	Percentage of the world production capacity	Percentage of ethane in total feedstock	Percentage of naphtha in total feedstock
Asia-Pacific	30	15	70
North America	24	71***	15***
West Europe	17	7	74
Middle East	17	59	24

*Calculated based on the data reported in [True 2013], **Extracted from [International Energy Agency Report 2007], ***Updated based on the new data revealing the increasing share of the shale gas in supplying the feedstock of ethane crackers [Lippe 2013]

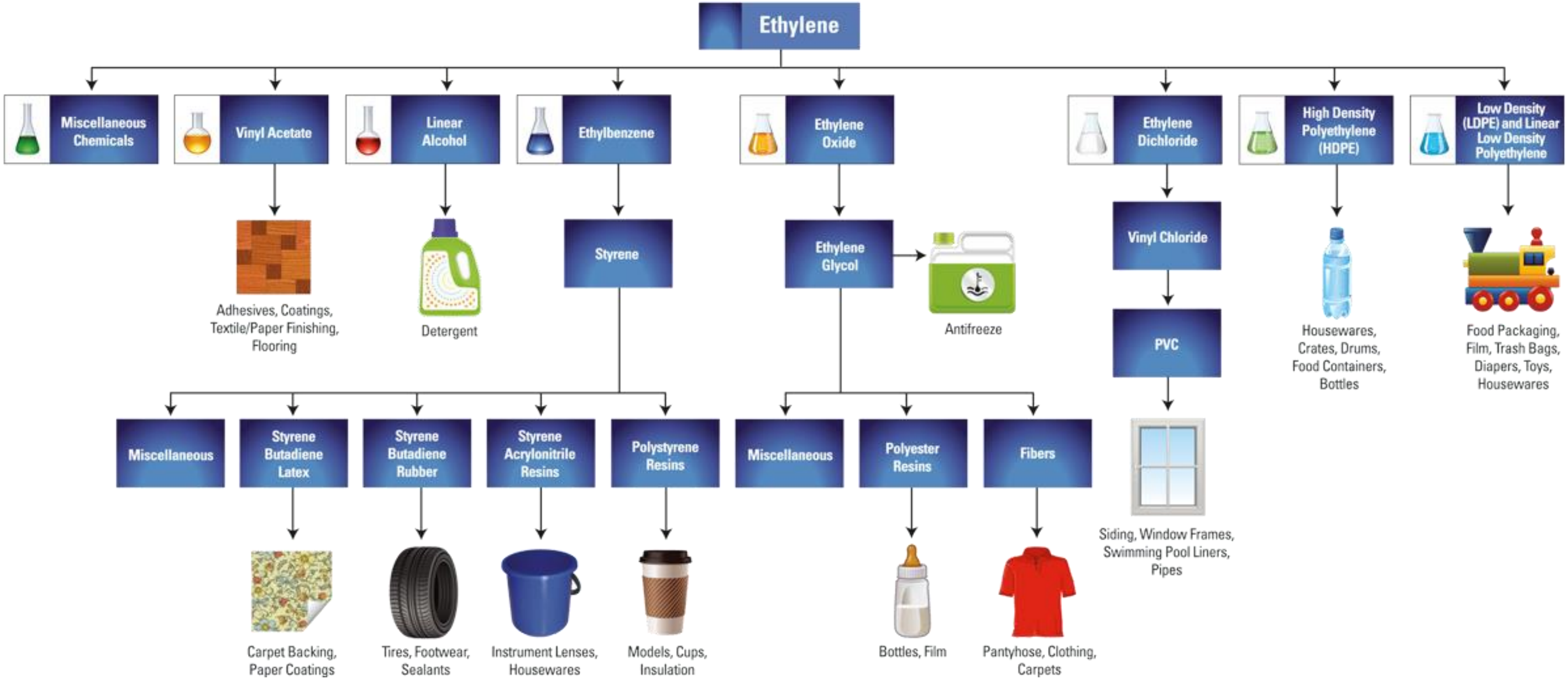

Figure 36. Derivatives and uses of Ethylene (source: http://www.energizewv.com/cracker)

Europe accounts today for nearly 20% of the global ethylene industry and it remains one of the largest markets for its derivatives, but it's suffering a constant decline in capacity and consumption: last year the trend of falling ethylene production continued, driven not only by weak domestic demand but also lower cost imports. Europe's ethylene industry is largely based on disadvantaged naphtha feedstock, causing domestic producers to lose out to their peers in the US and the Middle East, whose crackers primarily use ethane. Moreover, the (Western) European petrochemicals industry is caught between the crisis in its markets (including the auto industry) and its higher material procurement costs.

As a result, ethylene, crucial for the whole plastics industry, was 1,5 times as expensive in Europe as in the United States in 2012. In order to address this negative trend, the EU industry is currently restructuring in order to achieve long-term survival: local producers are attempting to shift to lighter feedstocks to improve their cost position, however this is not an easy task as hurdles such as infrastructure, geographic location, co-product requirements and supply contracts could limit flexibility. Consequently, the difficult conditions have led to ethylene plant closures of over two million tons, with demand having fallen by around 3Mln tons [41].

The DEMCAMER project intended to concretely contribute to the improvement of the above-mentioned condition of the EU industry, by making a viable a more economic and efficient route for ethylene production, thus promising to re-establish the European position globally.

Benefits of producing Ethylene from natural gas

With an oil-to-gas price stably over 3 (even in these days of low oil price), it becomes more and more attractive to convert methane to higher hydrocarbons (including C_2) that are conventionally produced by cracking of oil (fractions). Additionally, a large amount of natural gas is annually wasted as it is produced in remote areas where its conversion with conventional systems or its transportation is uneconomical. Worldwide many anti-flaring regulations are introduced. This market is expected to grow between 2020-2030 and no economic solutions are available. Many current developments still work on centralized solutions, combining many sources of associated gas into one stream with high CAPEX costs.

The sum of these factors clearly shows the high potential of the use of methane for ethylene production as a highly promising and concrete alternative for the EU process industry.

DEMCAMER project must offer a series of benefits in order to commercialize its products. The following table describes how DEMCAMER globally could contribute towards economic impacts:

Table 7. Economic impacts.

Products	Production Volume	Cost	Economical Impact
Hydrogen	➢ 50 MT/y (2004, Global) (EU 16%, USA 21%)[xv] Expected increase in the next 40 years: >750%	3200-4000 €/T[xvi]	1500-2000 €/T (2015)[xvii]
Ethylene	➢ 132 MT/y (2008, Global)[xviii]. Expected in 2020, 300 MT/y	800-900 €/T(2009)[xix]	IRR(OCM-CMR) = 27.7 % > 22 % = IRR(conventional)[xx]
FTS-diesel	➢ 0.2 Mbpd (2006)[xxi], Expected production 1.6 Mbpd (2030)	15 – 20 €/b.[xxii]	7.5 - 10 €/b.

These expected impacts and economic benefits brought by the DEMCAMER approach could allow convincing the conservative chemical sector about the benefits of CMR. The previous economic impacts will be reached by:

➢**Novel materials solutions: *Cheaper materials* (membranes and catalysts). *Cheap manufacturing method* with the potential of mass production** ➢**New Catalytic Membrane Reactors concepts design.** ➢**Reduced capital cost: CMR technology is expected to have cost savings from 25 to 50% depending on process (i.e. WGS-CMR cost reduction 35-45%).**	➢**Low energy cost: higher conversion at low temperature and better energy integration (e.g. net electrical efficiencies about 9% for SR and WGS-CMRs).** ➢**Low operation and maintenance costs: Simpler operation. Stable materials under severe process conditions.** ➢**Inexpensive CO_2 separation (depending on the process <50%, around 20-30 €/T CO_2 captured).**

But DEMCAMER results could be exploited in many other industrial sectors as detailed below:

Table 8. DEMCAMER results and other exploitation areas.

Results	Potential applications
Advanced materials and membranes	➢Direct application in Chemistry and related Industries (purification, separation, (gas separation, pervaporation, ultrafiltration, nanofiltration)). ➢Application in power plants and energy transformation (IGCC/NGCC + CCS, fuel cells). (IGCC: "Integrated Gasification Combined Cycle", NGCC: "Natural Gas Combined Cycle", CCS: Carbon capture and storage) ➢Applications in other industries: Water treatment, Aeronautic (OBOGGS), Automotive, Metallurgy, Food, Health, Electronic. ➢Seals for high temperature and pressures applications, other industries (ceramics, furnace, energy-SOFC-Fuel Cells)
New catalysts materials	➢Direct applications in ATR, WGS, FTS, OCM, SMR, Catalytic Partial Oxidation. ➢Applications in other industries: new method of catalysts application (e.g. energy) ➢Direct application in compact reformers
Optimized materials processing techniques	➢Potential application for manufacturing other innovative membranes and membrane modules (MF,UF,NF,PV) (e.g. manufacturing flexible porous hollow fibres, deposition of thin membranes on complex support geometries). Applications in other industries: ▪ Potential coating synthesis technique for synthesis of hard and wear resistant coatings (as on cutting tools, forming tools, etc.) ▪ Potential coating technique for synthesis of oxides and TCOs for the solar industry (solar concentrators, photovoltaic, etc.) ▪ Potential coating technique based on detonation spraying for the cost-competitive manufacture of thin solid oxide layers for application as electrolytes, seals and bipolar-plates in fuel cells and electrolysers.
New reactor design and processes	➢To extend the new design concepts towards other markets using intensified reactors. (e.g. oxidative, dehydrogenation hydrogenation reactions, VOCs, NO_X, SO_X) ➢Health & safety, environmental engineering, chemicals, recycling industries. ➢To extend the micro-reactor design of an WGS-CMR to other reactions. ➢New processes for clean synthetic fuels
Modelling of reaction systems	➢To extend the operating windows of membrane reactors to be used in different applications (e.g. miniaturization for pure hydrogen production on site in residential-automotive sectors, exploitation in areas of catalyst design,…) ➢To provide information about the relative stability of the different structures, guiding the synthetic route to the most stable combinations. ➢To develop a new tool able to predict the performance of the catalytic membrane reactors cutting a lot of experimental effort.

Associated community societal objectives

Employment: Under the risk that the EU chemical industry could become soon a net importer of chemicals, SusChem outlined strategic R&D strategies aimed to help this sector in maintaining a large global share. DEMCAMER will contribute herewith by providing decisive step-changes in the bulk chemical industry that will not only safeguard its global market position and employment but also enable it to enter new markets and create new workplaces.

Quality of life & Health:

- ✓ Production cost savings of ~ 50% in 1st stage products will reach downstream suppliers of daily commodity goods (e.g. petrochemical, plastics) in the short-medium term.
- ✓ Smaller and more compact CMRs, with lower hazardous inventories, will lead to safer and more comfortable working conditions.
- ✓ Innovations in water membranes will positively impact the water treatment sector.

Environmental impact:

- ✓ More efficient use of raw material resources and minimization of by-products formation (less wastes) due to the high selectivity and conversion rates.
- ✓ CO_2 capture/storage is an essential factor for fossil fuels to be part of the sustainable energy scenario, but is associated with high costs (capture ~70-80% of total costs). One primary EU objective is to decrease the capture costs from 50-60 to 20-30 €/t CO_2. DEMCAMER will contribute by developing reactors with intrinsic CO_2 capture, thus reducing the needs for downstream steps. These factors will allow a reduction in the global energy consumption of at least 7%.
- ✓ Fostering of green transportation and energy supply technologies due to lower H_2 prices.

Dissemination activities

Actions were undertaken to create awareness of the DEMCAMER project, its objectives and anticipated and achieved results. These actions were carried on, continued through the whole project duration and are in progress after the project end as well. In addition, to the specific ones listed later on, they include

i) **Publications in scientific journals**. Overall DEMCAMER has already published more than 32 articles in peer-reviewed journals and there are still request for further publications. A detailed list is reported in Section A.

ii) **Major international and national conferences** attended by DEMCAMER participants and both poster and oral presentations given, as appropriate. Conferences attended in particular included regular events conducted in the frame of the above mentioned target groups and conferences organised or sponsored by organisations such as the "World Hydrogen Energy Conference" sponsored by the "International Association for Hydrogen Energy IAHE" (http://www.iahe.org). Also, industry fairs as ACHEMA (Germany)) etc., have been attended by DEMCAMER participants. Important international conferences as e.g. the World Hydrogen Energy Conferences (2012 in Toronto, Canada) or the World Hydrogen Technology Conventions (2011 in Glasgow, Scotland) were also attended. Specific conferences related to the membrane reactors (i.e. International Conference on Catalysis in Membrane Reactors. Overall the consortium has contributed in more than 119 oral or poster presentation. A detailed list is reported in Section A.

iii) **Six monthly newsletters** on the project activities and dissemination. 8 newsletters have been released.

iv) **Non-confidential presentations**. 4 non-confidential presentations have been released.

v) **Brochure and poster presenting the projects** (including posters for main scientific and pilot pics).

vi) **Information letter** sent to platforms and national and international organizations to improve the visibility and the awareness of the project.

vii) **Contacting other consortia** working on projects related to the same R&D field for identifying common interests and joint activities.

viii) **The training, dissemination and/or exploitation workshops**. The following public workshops have been organised by DEMCAMER or jointly with other EC projects:
  - The one day internal Exploitation Strategy Seminar day before the M6 meeting in Mol (Belgium).
  - The scientific-oriented training workshop for PhD students and young researchers at Eindhoven, on January the 30th, 2013. The workshop has been organised by the two projects on membrane reactors granted by FP7 - Theme NMP: DEMCAMER and CARENA.
  - The technology oriented workshop has been organised with other EC funded projects that share similar technological challenges. CARENA, CoMETHy and ReforCELL. The two-day workshop was held at the Energy Research Centre of the Netherlands ECN, Petten, The Netherlands on 20th-21st of November 2014. The workshop brought together more than 70 participants from 17 countries with a broad participation of industrial stakeholders besides representatives of research institutions and universities.
  - The final dissemination and exploitation event which took place in Szezcin (Poland), on 22nd and 25th June 2015, as specific event during the International Conference on Catalysis in Membrane Reactors.

ix) **Thesis:** Five PhD thesis have been carried out in the frame of the DEMCAMER projects as well as ten MSc thesis.

x) **Public website**. A public website was available around month 4th. The website has been regularly updated with the latest news as well as the different public documents released by the consortium (i.e. public presentations, newsletters,…).

4.1.5. Project public website and contact

Project public website with further information of the about the project and consortium and main contacts details are detailed hereafter:

www.demcamer.org

Coordinator: Dr. José Luis Viviente
e-mail: joseluis.viviente@tecnalia.com

Scientific responsible: Associate Prof. Fausto Gallucci
e-mail: F.Gallucci@tue.nl

Dissemination manager: Prof. Enrico Drioli
e-mail: e.drioli@unical.it

Exploitation manager: Dr. Leonardo Roses
e-mail: leonardo.roses@hygear.nl

4.2. Use and dissemination of foreground

A plan for use and dissemination of foreground (including socio-economic impact and target groups for the results of the research) shall be established at the end of the project. It should, where appropriate, be an update of the initial plan in Annex I for use and dissemination of foreground and be consistent with the report on societal implications on the use and dissemination of foreground (section 4.3 – H).

The plan should consist of:

- Section A

This section should describe the dissemination measures, including any scientific publications relating to foreground. **Its content will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

- Section B

This section should specify the exploitable foreground and provide the plans for exploitation. All these data can be public or confidential; the report must clearly mark non-publishable (confidential) parts that will be treated as such by the Commission. Information under Section B that is not marked as confidential **will be made available in the public domain** thus demonstrating the added-value and positive impact of the project on the European Union.

Section A

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 publication	Year of publication	Relevant pages	Permanent identifiers[2] (if available)	Is/Will open access[3] provided to this publication?
1	Recent advances on membranes and membrane reactors for hydrogen production	F. Gallucci	Chemical Engineering Science	92	Elsevier Ltd.		2013	40-66	doi:10.1016/j.ces.2013.01.008	
2	Nanoscale control during synthesis of Me/La$_2$O$_3$, Me/Ce$_x$Gd$_{1-x}$O$_y$ and Me/Ce$_x$Zr$_{1-x}$O$_y$ (Me = Ni, Pt, Pd, Rh) catalysts for autothermal reforming of methane	I.Z. Ismagilov	Catalysis Today	210	Elsevier B.V.		2013	10-18	doi:10.1016/j.cattod.2012.12.007	
3	Organic-Template-Free Synthesis of Nano-sized NaY Crystals Induced by a FAU Membrane	T. Poerio	RCS Advances	3	RSC		2013	24038-24040	doi: 10.1039/C3RA43790F	
4	Zeolite membranes for hydrogen and water separation under harsh conditions	Ch. Günther	Chemical Engineering Transactions	32	AIDIC		2013	1963-1968	doi: 10.3303/CET1332328	
5	Ceramic Materials for Environmental and Energy Applications: Functionalizing of Properties by Tailored Compositions	M. Ivanova	Doping: Properties, Mechanisms and Applications	Chapter 6	Nova Science Publishers		2013	221-276	publica.fraunhofer.de/documents/N-278933.html ISBN: 978-1-62618-097-0	
6	Hydrogen production by	I.Z.	Applied	481	Elsevier		2014	104-115	doi:10.1016/j.apcata.2	

---

[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.

	autothermal reforming of methane: Effect of promoters (Pt, Pd, Re, Mo, Sn) on the performance of Ni/La_2O_3 catalysts	Ismagilov	Catalysis A: General		B.V.				014.04.042	
7	Resource scarcity in palladium membrane applications for carbon capture in integrated gasification combined cycle units	A. Helmi	International Journal of Hydrogen Energy	39	Elsevier Ltd.		2014	10498-10506	doi:10.1016/j.ijhydene.2014.05.009	
8	Low Temperature Synthesis of Nanosized NAY Zeolite Crystals from Organic-Free Gel by Using Supported Seeds.	T. F. Mastropietro	RCS Advances	4	RSC		2014	21951-21957	doi: 10.1039/C4RA03376K	
9	Energy and mass intensities in hydrogen upgrading by a membrane reactor	A. Brunetti	Fuel Processing Technology	118	Elsevier B.V.		2014	278-286	doi:10.1016/j.fuproc.2013.09.009	
10	Development And Characterisation Of Dense Lanthanum-Based Perovskite Oxygen-Separation Capillary Membranes For High-Temperature Applications	V. Middelkoop	Journal of Membrane Science	468	Elsevier B.V.		2014	250-258	doi:10.1016/j.memsci.2014.05.032	
11	Methane partial oxidation over a LaCr0.85Ru0.15O3 catalyst: Characterization, activity tests and kinetic modeling	T. Melchiori	Applied Catalist A: General	486	Elsevier B.V.		2014	239-249	doi:10.1016/j.apcata.2014.08.040	
12	Soft Synthesis of FAU Nanozeolites and Microporous Membranes	T. F. Mastropietro	Advances in Science and Technology	87	Trans Tech Publications		2014	24-29	DOI: 10.4028/www.scientific.net/AST.87.24	
13	Using palladium membrane-based fuel reformers for combined heat and power (CHP) plants	F. Gallucci	Palladium Membrane Technology for H2 Production, Carbon Capture and Other Applications	Chapter 15	Elsevier Ltd.		2015	319-344	doi:10.1533/9781782422419.2.319	
14	Membrane reactors for autothermal reforming of	A. Arratibel	Membrane Reactors for	Chapter 3	Elsevier Ltd.		2015	61-98	doi:10.1016/B978-1-78242-223-5.00003-0	

	methane, methanol, and ethanol		Energy Applications and Basic Chemical Production							
15	Auto-thermal reforming using mixed ion-electronic conducting ceramic membranes for a small-scale H2 production plant Molecules	V. Spallina	Molecules	20(3)	MDPI, Basel (Swtzerland)		2015	4998-5023	doi:10.3390/molecules20034998	
16	Large-scale ceramic support fabrication for palladium membranes	H. Richter	Palladium Membrane Technology for H2 Production, Carbon Capture and Other Applications	Chapter 4	Elsevier Ltd.		2015	69-82	doi:10.1533/9781782422419.1.69	
17	Development of thin Pd–Ag supported membranes for fluidized bed membrane reactors including WGS related gases	E. Fernandez	International Journal of Hydrogen Energy	40	Elsevier Ltd.		2015	3506-3519	doi:10.1016/j.ijhydene.2014.08.074	
18	Adsorption properties and permeation performances of DD3R zeolite membranes	A. Caravella	Chemical Engineering Transactions	43	AIDIC		2015	1075-1080	doi: 10.3303/CET1543180	
19	Reactive air brazing for sealing mixed ionic electronic conducting hollow fibre membranes	H. Chen	Acta Materialia	88	Elsevier Ltd.		2015	74-82	doi:10.1016/j.actamat.2015.01.029	
20	Real time chemical imaging of a working catalytic membrane reactor during oxidative coupling of methane	A. Vamvakeros	Chemical Communications	51	RSC		2015	12752-12755	doi: 10.1039/C5CC03208C	
21	Evaluation of Pure-Component Adsorption Properties of DD3R based on the Langmuir and Sips Models	A. Caravella	Journal of Chemical & Engineering Data	60	ACS Publications		2015	2343-2355	doi: 10.1021/acs.jced.5b00252	
22	Syngas upgrading in a membrane reactor with thin Pd-alloy	A. Brunetti	Intern. Journal of Hydrogen	40	Elsevier Ltd.		2015	10883-10893	doi:10.1016/j.ijhydene.2015.07.002	

	supported membrane		Energy							
23	Synthesis of NAY-type nanozeolites and their assembling into microporous membranes	T.F. Mastropietro	Chemical Engineering Transactions	43	AIDIC		2015	715-720	DOI: 10.3303/CET1543120	
24	New high temperature sealing technique and permeability data for hollow fiber BSCF perovskite membranes	L. Di Felice	Chemical Engin. and Processing: Process Intensification		Elsevier B.V.		2015, In Press (Available online)		doi:10.1016/j.cep.2014.12.004	
25	Evaluation of Pure-Component Adsorption Properties of Silicalite based on the Langmuir and Sips Models	A. Caravella	AIChE Journal		AIChE		2015, In Press (Available online)		doi: 10.1002/aic.14925	
26	Estimation of Langmuir and Sips Models Adsorption Parameters for NaX and NaY FAU Zeolites	P. F. Zito	Journal of Chemical & Engin. Data		ACS Publications		2015, Submitted			
27	In situ Crystallization and Assembling of FAU Nanozeolites Membranes on Ceramic Supports	T.F. Mastropietro	Microporous and Mesoporous Materials		Elsevier Inc.		2015, Submitted			
28	Study of the Separation Properties of FAU Membranes Constituted by Hierarchically Assembled Nanozeolites.	T.F. Mastropietro	Separation and Purification Technology		Elsevier B.V.		2015, Submitted			
29	Identifying the active sites for the Fischer-Tropsch synthesis via selective knockout of step-edge sites	D. Liuzzi					2015, Submitted			
30	Catalytic membrane reactors for the production of biofuels	D. Liuzzi					2015, To be submitted			
31	Pt-Re/CeO2-TiO2 WGS catalyst for membrane reactors	V. del Villar					2015, Submitted			
32	Effect of Re addition on the WGS activity and stability of Pt/CeO2-TiO2 catalyst for membrane reactor applications	V. del Villar	Catalysis Today		Elsevier B.V.		2015, Submitted			

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES

NO.	Type of activities[4]	Main leader	Title	Date /Period	Place	Type of audience[5]	Size of audience (no. partecipants)	Countries addressed
1	*Poster - Development of laboratory setup for oxidative methane conversion processes*	BIC	*International conference “Nanostructured catalysts and catalytic processes for the innovative energetics and sustainable development”*	2011 June 5-8	Novosibirsk (Russia)	Scientific community; Industry	100 ca.	European Countries; etc
2	*Poster - Presentation of DEMCAMER project*	TECNALIA	ICOM 2011 - International Conference on Membranes and membrane processes	2011 July 23-29	Amsterdam (The Netherland)	Scientific community; Industry	1000 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
3	*Poster - Thermal and hydrothermal stability of sodalite membranes depending on the seeding*	IKTS	Deutsche Zeolith-Tagung	2012 March 7-9	Magdeburg (Germany)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
4	*Poster - Fabrication of Dense Mixed Ionic-Electronic Conducting (MIEC) Perovskite Capillaries for High-Temperature Oxygen Separation*	VITO	IMETI&CARENA workshop	2012 March 27-28	Montpellier (France)	Scientific community; Industry	200 ca.	European Countries; etc
5	*Poster - Presentation of DEMCAMER project*	TECNALIA	IMETI&CARENA workshop	2012 March 27-28	Montpellier (France)	Scientific community; Industry	200 ca.	European Countries; etc.
6	*Oral presentation - Robust gas separation porous ceramic membranes*	IKTS	i-SUP 2012	2012 May 6-9	Bruges (Belgium)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.

---

[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.

7	*Oral presentation -Composite palladium membranes with improved durability by electroless plating*	TECNALIA	i-SUP 2012	2012 May 6-9	Bruges (Belgium)	Scientific community; Industry	400 ca.	European Countries; etc.
8	*Oral presentation - Synthesis and study of catalysts for autothermal methane reforming based on* Ni/La_2O_3	BIC	*All-Russia school-conference for young scientists "Chemistry under sigma sign - research, innovations, technologies"*	2012 May 14-22	Omsk (Russia)	Scientific community; Industry	100 ca.	European Countries; etc.
9	*Poster - Synthesis and study of catalysts for oxidative coupling of methane based on* $Na\text{-}W\text{-}Mn/SiO_2$	BIC	*Chemistry under sigma sign - research, innovations, technologies*	2012 May 14-22	Omsk (Russia)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
10	*Oral presentation - Development of MIEC Ceramic Membranes for Gas Separation and Catalytic Membrane Reactors*	VITO	CMCEE - 10th International Symposium on Ceramic Materials and Components for Energy and Environmental Applications	2012 May 20-23	Dresden (Germany)	Scientific community; Industry	400 ca.	European Countries; etc.
11	*Thermal and hydrothermal stable zeolite membranes for* H_2*-separation*	IKTS	CMCEE - 10th International Symposium on Ceramic Materials and Components for Energy and Environmental Application	2012 May 20-23	Dresden (Germany)	Scientific community; Industry	400 ca.	European Countries; etc.
12	*Poster - Presentation of DEMCAMER project*	VITO	CMCEE - 10th International Symposium on Ceramic Materials and Components for Energy and Environmental Applications	2012 May 20-23	Dresden (Germany)	Scientific community; Industry	400 ca.	European Countries; etc.
13	*Oral presentation - One-stage Process of Water Gas Shift in a Pd-based Membrane Reactor – Mention of DEMCAMER prohect*	UNICAL	ACHEMA 2012	2012 June 18-22	Frankfurt (Germany)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.

14	*Poster - Inorganic Membranes for High-Temperature Gas Separation and Catalytic Membrane Reactors*	VITO	ACHEMA 2012	2012 June 18-22	Frankfurt (Germany)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
15	*Poster - Presentation of DEMCAMER project*	VITO	ACHEMA 2012	2012 June 18-22	Frankfurt (Germany)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
16	*Poster - Presentation of DEMCAMER project*	TECNALIA	INDUSTRIAL TECHNOLOGIES 2012	2012 June 19-21	Aarhus (Denmark)	Scientific community; Industry	800 ca.	European Countries, etc
17	*Poster - Presentation of DEMCAMER project*	TECNALIA	ANQUE-ICCE 2012	2012 June 24-27	Seville (Spain)	Scientific community; Industry	600 ca.	European Countries; etc
18	*Oral presentation - Membranes for gas separation*	TECNALIA	ANQUE-ICCE 2012	2012 June 24-27	Seville (Spain)	Scientific community; Industry	600 ca.	European Countries; etc
19	*Poster - Pt/CeO_x-TiO_2 catalysts for the WGS reaction: effect of catalysts preparation on catalysts structure and activity – Mention of DEMCAMER project*	ICP-CSIC	Catalysis for Clean Energy and Sustainable Chemistry 2012	2012 June 27-29	Madrid (Spain)	Scientific community; Industry	400 ca.	European Countries; etc.
20	*Poster - Oxidative coupling of methane: comparative study on Na-W-Mn/SiO_2 and La-Sr/CaO catalysts-Mention of DEMCAMER project*	BIC	Catalysis for Clean Energy and Sustainable Chemistry 2012	2012 June 27-29	Madrid (Spain)	Scientific community; Industry	400 ca.	European Countries; etc.
21	*Oral presentation - Nanoscale control during synthesis of Me/La2O3, Me/CexGd1-xOy and Me/CexZr1-xOy (Me = Ni, Pt, Pd, Rh) catalysts for autothermal reforming of methane – Mention of DEMCAMER project*	BIC	Catalysis for Clean Energy and Sustainable Chemistry 2012	2012 June 27-29	Madrid (Spain)	Scientific community; Industry	400 ca.	European Countries; etc.
22	*Poster - Autothermal reforming of methane over modified*	BIC	Catalysis for Clean Energy and Sustainable	2012 June 27-29	Madrid (Spain)	Scientific community;	400 ca.	European Countries; China, South Korea;

	lanthanum chromites		Chemistry 2012			Industry		India; Iran; Israel; USA; etc.
23	*Oral presentation - Fabrication of Dense Mixed Ionic-Electronic Conducting (MIEC) Perovskite Capillary Membranes for High-Temperature Oxygen Separation*	VITO	AMS7 - 7th Conference of Aseanian Membrane Society)	2012 July 4-6	Busan (South Korea)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
24	*Oral presentation - Development of Dense Mixed Ionic-Electronic Conducting (MIEC) Ceramic Capillaries for High-Temperature Oxygen Separation*	VITO	ISIM4 - 4th International Symposium on Inorganic Membranes	2012 July 7	Daejeon (South Korea)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
25	*Poster - FAU Zeolite Membranes for Gas Separation*	UNICAL	International Conference on Inorganic Membranes	2012 July 9-13	Enschede (The Netherlands)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
26	*Poster - Hydrothermal stable sodalite membranes for gas separation*	IKTS	International Conference on Inorganic Membranes	2012 July 9-13	Enschede (The Netherlands)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
27	*Poster - Development of catalyst for oxidative coupling of methane in a catalytic membrane reactor*	BIC	ICEC 2012 - International Conference on Environmental Catalysis	2012 September 2-6	Lyon (France)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
28	*Poster - Design of efficient catalyst for autothermal methane reforming*	BIC	ICEC 2012 - International Conference on Environmental Catalysis	2012 September 2-6	Lyon (France)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
29	***Invited lectures*** *- Zeolithmembranen – Stand der Entwicklung und Anwendung*	IKTS	ProcessNet-Jahrestagung und 30. Jahrestagung der Biotechnologen	2012 September 10-13	Karlsruhe (Germany)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
30	*Poster - Syngas upgrading by high temperature WGS reaction in a single stage membrane*	UNICAL	Euromembrane 2012	2012 September 23-27	London (UK)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel;

	reactor							USA; etc.
31	*Poster - Synthesis of FAU-Type Zeolite Membrane for Gas Separation*	UNICAL	Euromembrane 2012	2012 September 23-27	London (UK)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
32	*Oral presentation - Peculiarities of oxidative coupling of methane on $Mn/Na_2WO_4/SiO_2$ u La/Sr/CaO catalysts – Mention of DEMCAMER project*	BIC	International Conference "Chemistry of oil and gas"	2012 September 24-28	Tomsk (Russia)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
33	*Oral presentation - Reactive Air Brazing of Mixed Ionic and Electronic Conducting Ceramic Membrane Materials to Metal or Ceramic Components*	VITO	Materials Science & Technology Conference and Exhibition (MS&T-12 - combined with ACerS 114th annual meeting)	2012 October 7-11	Pittsburgh (USA)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
34	*Poster - Effect of B-cation substitution on the activity of $LaCrO_3$ and $LaNiO_3$ perovskites for autothermal reforming of methane*	BIC	MCR 2012 - International Conference "Mechanisms of Catalytic Reactions"	2012 October 22-25	St. Petersburg (Russia)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
35	*Poster - Comparative study of oxidative coupling of methane to ethane and ethylene over Na-W-Mn/SiO_2 and La-Sr/CaO catalysts*	BIC	MCR 2012 - International Conference "Mechanisms of Catalytic Reactions"	2012 October 22-25	St. Petersburg (Russia)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
36	*Oral presentation - One-stage Process for Water Gas Shift in a Pd-based Membrane Reactor*	UNICAL	AIChE Annual Meeting	2012 October 28 - November 2	Pittsburgh (USA)	Scientific community; Industry	300 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
37	***Invited lecture** - Large scale ceramic membranes fabrication*	IKTS	Pd Membrane Technology Scale-up Workshop	2012 November 12-14	Rome (Italy)	Scientific community; Industry	100 ca.	European Countries; etc
38	*Oral presentation -Preparation of supported Pd alloy membranes*	TECNALIA	Pd membrane technology scale-up workshop	2012 November 12-14	Rome (Italy)	Scientific community; Industry	100 ca.	European Countries; etc
39	*Poster - Trennmechanismen von Zeolithmembranen am*	IKTS	XVI. Workshop über die Charakterisierung von	2012 November	Bad Soden (Germany)	Scientific community;	100 ca.	European Countries; China, South Korea;

	Beispiel der H_2/CO_2-Trennung		feinteiligen und porösen Festkörpern, Transport in porösen Medien	13-14		Industry		India; Iran; Israel; USA; etc.
40	***Invited lecture** - Preparation of Catalysts*	CSIC	CARENA-DEMCAMER workshop	2013 January	Eindhoven	Scientific community; Industry	100 ca.	European Countries;
41	*Poster - Development of Ru core-shell based catalysts for Fischer-Tropsch Synthesis to be used in a new concept of membrane reactors*	CSIC	CARENA-DEMCAMER workshop	2013 January	Eindhoven (The Netherlands)	Scientific community; Industry	100 ca.	European Countries;
42	*Pt/CeOx-TiO2 catalysts for WGS: effect of preparation conditions on structure and activity*	CSIC	CARENA-DEMCAMER workshop	2013 January	Eindhoven (The Netherlands)	Scientific community; Industry	100 ca.	European Countries;.
43	***Invited lecture** - Membrane Reactors for Chemistry and Energy Applications*	VITO	Membrane technology course: Membraantechnologie - van theorie tot praktijk	2013 February 26-28	Mol (Belgium)	Scientific community;	100 ca.	European Countries;
44	*Poster - Microwave synthesis of stabilized sodalite for hydrogen separation*	IKTS	Deutsche Zeolithtagung	2013 March 6-8	Hamburg (Germany)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
45	*Oral presentation - Micro-structured membrane reactors for water gas shift reaction*	TUE	21st Process Intensification Network Meeting	2013 May 23	Newcastle (UK)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
46	*Oral presentation - Zeolite membranes for hydrogen and water separation under harsh conditions*	IKTS	11th Intern. Conf. on Chemical Process Engineering	2013 June 2-5	Milan (Italy)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
47	*Poster - Stabilization of SOD for H_2- and H_2O-separating membranes of high resistance in thermal and hydrothermal conditions*	IKTS	IZMM-6 - 6th International Zeolite Membrane Meeting	2013 June 15-19	Jeju Island (Korea)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
48	*Oral presentation - Membrane*	TUE	ICCMR11 - 11th	2013	Porto (Portugal)	Scientific	200 ca.	European Countries;

	assisted fluidized bed reactor for water gas shift reaction		International Conference on Catalysis in Membrane Reactors	July 7-11		community; Industry		China, South Korea; India; Iran; Israel; USA; etc.
49	*Oral presentation - Non conventional analysis of the performance of a membrane reactor for hydrogen upgrading*	UNICAL	ICCMR11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
50	*Poster - One-stage Process of Water Gas Shift with a Pd-Ag membrane reactor*	UNICAL	ICCMR11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
51	*Oral presentation - Simultaneous autothermal reforming of methane (ATR) and O2 separation via hollow fibre perovskite membranes in a membrane reactor: experimental data and reactor modeling*	TUE	ICCMR11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
52	*Invited tandem lecture - Membrane reactors in FP7, experience from DEMCAMER and CARENA*	TUE	ICCMR11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
53	*Poster - Surface modification of La0,6Sr0,4Co0,2Fe0,8O3-δ hollow fiber membranes for oxygen separation*	VITO	ICCMR11 – 11th International Conference on Catalytic Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
54	*Oral presentation - Preparation and characterization of thin Pd based membranes supported on porous alumina tube by PVD Magnetron Sputtering*	TECNALIA	ICCMR 11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
55	*Poster - Preparation and characterization of intermetallic diffusion barrier layers for stainless steel supported*	TECNALIA	ICCMR 11 - 11th International Conference on Catalysis in Membrane Reactors	2013 July 7-11	Porto (Portugal)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.

	palladium membranes							
56	*Poster - Sulfur stabilized sodalite for membrane applications*	IKTS	17th International Zeolite Conference	2013 July 7-12	Moscow (Russia)	Scientific community; Industry	150 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
57	*Poster - Presentation of DEMCAMER project*	TECNALIA	Inorganic Membranes Summer School	2013 September 4-6	Valencia (Spain)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
58	*Oral presentation - Preparation and characterization of Palladium membranes for hydrogen separation-Mention of DEMCAMER project*	TECNALIA	Inorganic Membranes Summer School	2013 September 4-6	Valencia (Spain)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
59	***Invited lectures** - Zeolite membranes for energy efficient separations in bio processes and power generation Inorganic membranes for green chemical production and clean power generation*	IKTS	Inorganic Membranes Summer School	2013 September 4-6	Valencia (Spain)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
60	*Poster - Highly Pure Hydrogen Production in a Micro-Channel Membrane Reactor for Fuel Cell Applications – Modeling and Experimental Work*	TUE	WHTC2013 - The Fifth World Hydrogen Technologies Convention	2013 September 25-28	Shanghai (China)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
61	*Oral presentation - Novel Membrane Reactor Concepts for Hydrogen Production*	TUE	WHTC2013 - The Fifth World Hydrogen Technologies Convention	2013 September 25-28	Shanghai (China)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
62	*Oral presentation - Preparation of supported Pd based membranes for hydrogen separation-Mention of DEMCAMER project*	TECNALIA	WHTC2013 - The Fifth World Hydrogen Technologies Convention	2013 September 25-28	Shanghai (China)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
63	*Development of Mixed Conducting Perovskite*	VITO	Engineering of Membrane Reactors for the Process	2013 October 3-6	Sarteano (Italy)	Scientific community;	100 ca.	European Countries;

	Membranes for High-Temperature O2 and H2 Separation and Catalytic Membrane Reactors		Industry			Industry		
64	***Invited lectures*** *- Ceramic membranes for separation on molecular level*	IKTS	ICMA 2013 - International Conference on Membranes and Applications	2013 November 22-23	Kolkata (India)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
65	*Poster - Organic-Template-Free Synthesis of NAY Nanosized Zeolites and Their Assembling into Microporous Membrane Layers*	UNICAL	Early-stage and Experiences Researchers Seminars, ITM-CNR	2013 December 18-19	Arcavacata di Rende (Italy)	Scientific community; Industry	70 ca.	Italy; European Countries; China, South Korea; India; Iran; etc.
66	*Poster - Gas Transport Evaluation Through Zeolite Membrane*	UNICAL	Early-stage and Experiences Researchers Seminars, ITM-CNR	2013 December 18-19	Arcavacata di Rende (Italy)	Scientific community; Industry	70 ca.	Italy; European Countries; China, South Korea; India; Iran; etc.
67	*Poster - Permeation of Gas Mixtures through Tubular Zeolite Membranes: Modeling Analysis and Simulation*	UNICAL	Early-stage and Experiences Researchers Seminars, ITM-CNR	2013 December 18-19	Arcavacata di Rende (Italy)	Scientific community; Industry	70 ca.	Italy; European Countries; China, South Korea; India; Iran; etc.
68	*Poster - Structure investigation of a sulfur containing hydroxysodalite without chromophores like sulfur radical anions*	IKTS	Deutsche Zeolithtagung	2014 February 26-28	Paderborn (Germany)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
69	*Poster - Preparation of Pd-Ag pore filled membranes for hydrogen separation*	TECNALIA	European Hydrogen Energy Conference 2014, EHEC 2014	2014 March 12-14	Seville (Spain)	Scientific community; Industry	200 ca.	European Countries
70	*Oral presentation - FAU Membrane for Organic-Template-Free Synthesis of Nanosized Zeolite Crystals*	UNICAL	13th International Ceramic Congress, CIMTEC	2014 June 8-13	Montecatini Terme (Italy)	Scientific community; Industry	150 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
71	*Flash oral- Pt/CeOx-TiO2 catalysts for WGS reaction: effect of preparation on the structure and activity*	CSIC	1st Symposium of Young Scientist of the Catalysis Spanish Society	2014 June	Torremolinos (Spain)	Scientific community; Industry	100 ca.	European Countries; etc.

72	*Oral presentation - Characterisation of Mixed Ionic-Electronic Conducting (MIEC) capillaries for high-temperature applications in a membrane reactor*	VITO	13th International Conference on Inorganic Membranes	2014 July 6-9	Brisbane (Australia)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
73	*Oral presentation - Fluidized bed membrane reactors for H2 production using thin Pd-Ag supported membranes*	TUE	13th International Conference on Inorganic Membranes	2014 July 6-9	Brisbane (Australia)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
74	*Poster - Fluidized bed water gas shift membrane reactor using thin Pd-Ag supported membranes - modeling and experimental work*	TUE	13th International Conference on Inorganic Membranes	2014 July 6-9	Brisbane (Australia)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
75	*Oral presentation - Nanoporous inorganic membranes for high temperature water separation*	IKTS	ICIM - 13th International Conference on Inorganic Membranes	2014 July 6-9	Brisbane (Australia)	Scientific community; Industry	400 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
76	*Poster - Predictive ab-initio study on the selectivity of crystalline nano-porous materials with respect to light gases*	UNICAL	ICOM 2014 - International Conference on Membranes and membrane processes	2014 July 20 -25	Suzhou (China)	Scientific community; Industry	1000 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
77	*Poster- Hydrogen trapping in metal alloys used membrane separations*	UNICAL	ICOM 2014 - International Conference on Membranes and membrane processes	2014 July 20 -25	Suzhou (China)	Scientific community; Industry	1000 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
78	*Oral presentation - Permeation performances and adsorption properties of DD3R zeolite membranes*	UNICAL	21st International Congress of Chemical and Process Engineering CHISA 2014	2014 August 23-27	Prague (Czech Republic)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
79	*Oral presentation - Soft synthesis of FAU nanozeolites and microporous membranes*	UNICAL	XXV National Congress of the Italian Chemical Society	2014 September 7-12	Arcavacata di Rende (Italy)	Scientific community; Industry	800 ca.	Italy
80	*Poster - Microporous FAU Y-type membranes*	UNICAL	XXV National Congress of the Italian Chemical	2014 September	Rende (Italy)	Scientific community;	800 ca.	Italy

			Society	7-12		Industry		
81	*Poster - Permeation performances of light gases through DD3R zeolite membranes*	UNICAL	XXV National Congress of the Italian Chemical Society	2014 September 7-12	Rende (Italy)	Scientific community; Industry	800 ca.	Italy
82	*Poster - Pd-Ag supported membranes for fluidized bed*	TUE	NPS14 conference	2014 November 3-5	Utrecht (The Netherlands	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
83	*Oral presentation - Concentration Polarisation and Inhibition by CO in Supported Pd-based Membrane*	UNICAL	Joint Workshop on Scale-up of Pd Membrane Technology From Fundamental Understanding to Pilot Demonstration	2014 November 20-21	Petten (The Netherlands)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
84	*Oral presentation - Membrane reactors innovating hydrogen stream upgrading*	UNICAL	Joint Workshop on Scale-up of Pd Membrane Technology From Fundamental Understanding to Pilot Demonstration	2014 November 20-21	Petten (The Netherlands)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
85	*Oral presentation - How membrane reactor can affect hydrogen production*	UNICAL	Joint Workshop on Scale-up of Pd Membrane Technology From Fundamental Understanding to Pilot Demonstration	2014 November 20-21	Petten (The Netherlands)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
86	*Development of Pd-based supported membranes*	TECNALIA	Joint Workshop on Scale-up of Pd Membrane Technology From Fundamental Understanding to Pilot Demonstration	2014 November 20-21	Petten (The Netherlands)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
87	*Poster - Preparation of Pd-based supported membranes by direct PVD deposition*	TECNALIA	Joint Workshop on Scale-up of Pd Membrane Technology From Fundamental	2014 November 20-21	, The Netherlands	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.

			Understanding to Pilot Demonstration					
88	*Poster - Pure-Component Adsorption Properties of Silicalite*	UNICAL	ITM Seminar Days	2014 December 17-18	Arcavacata di Rende (Italy)	Scientific community; Industry	70 ca.	Italy
89	*How membrane reactors can affect hydrogen production*	UNICAL	ITM Seminar Days	2014 December 17-18	Arcavacata di Rende (Italy)	Scientific community; Industry	70 ca.	Italy
90	*Poster - Observing the solid-state chemistry inside a working catalytic membrane reactor*	TUE	UKCC2015 - Inaugural UK Catalysis Conference	2015 January 8-9	Loughborough (UK)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
91	*Oral presentation - Observing the solid-state chemistry inside a working catalytic membrane reactor*	TUE	UKCC2015 - Inaugural UK Catalysis Conference	2015 January 8-9	Loughborough (UK)	Scientific community; Industry	120 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
92	*Observing the solid-state chemistry inside a working catalytic membrane reactor*	TUE	5th International Conference on Operando Spectroscopy	2015 May 17-21	Deauville (France)	Scientific community; Industry	200 ca.	European Countries; etc.
93	*Langmuir and Sips parameters laws estimated for Pure-Component Adsorption on NaX and NaY FAU zeolite*	UNICAL	7th International Conference on Porous Media & Annual Meeting	2015 May 18-21	Padova (Italy)	Scientific community; Industry	70 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
94	*Oral presentation - New advances on membrane reactors for hydrogen production - Mention of DEMCAMER project*	TUE	23rd Process Intensification Network Meeting	2015 May 20	Newcastle (UK)	Scientific community; Industry	100 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
95	*Oral presentation - High temperature water gas shift in innovative packed bed membrane reactor*	UNICAL	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
96	*Oral presentation - On the concentration polarization in packed bed and fluidized bed membrane reactors*	UNICAL	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
97	*Oral presentation -*	TUE	ICCMR12 - 12th	2015	Szczecin (Poland)	Scientific	200 ca.	European Countries;

	Development and characterisation of catalytic membrane reactors for oxidative coupling of methane		International Conference on Catalysis in Membrane Reactors	June 22-25		community; Industry		China, South Korea; India; Iran; Israel; USA; etc.
98	*Oral presentation - Observing the chemical evolution of a working catalytic membrane reactor*	TUE	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
99	*Oral presentation - Presentation of DEMCAMER project*	TECNALIA	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
100	*Oral presentation - Preparation and characterization of ultra-thin (<1 μm) palladium-silver membranes – Mention of DEMCAMER project*	TECNALIA	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
101	*Oral presentation - Catalytic membrane reactors for the production of biofuels*	CSIC	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
102	*Oral presentation - On membrane preparation for high temperature membrane reactors*	TUE	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
103	*Oral presentation - Metallic Supported palladium alloy membranes for high temperature (fluidized bed) applications*	TUE	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
104	*Oral presentation - Development and characterization of Catalytic membrane reactors for oxidative coupling of methane*	VITO	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
105	*Oral presentation - Observing the chemical evolution of a*	TUE	ICCMR12 - 12th International Conference	2015 June 22-25	Szczecin (Poland)	Scientific community;	200 ca.	European Countries; China, South Korea;

	working catalytic membrane reactor		on Catalysis in Membrane Reactors			Industry		India; Iran; Israel; USA; etc.
106	*Oral presentation - Optimization of membrane reactors for fischer tropsch synthesis*	TUE	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
107	*Poster - Advanced Pt-Re/CeO2-TiO2 WGS Catalyst For Membrane Reactor Applications*	CSIC	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
108	*Oral presentation - Integrated Membrane System For Hydrogen Production*	UNICAL	ICCMR12 - 12th International Conference on Catalysis in Membrane Reactors	2015 June 22-25	Szczecin (Poland)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
109	*NaY-type Faujasite Membranes for Light Gas Separation: Modelling and Simulation*	UNICAL	ZMPC2015 - International Symposium on zeolite and microporous crystals	2015 June 28-July 2	Sapporo (Japan)	Scientific community; Industry	180 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
110	*Authothermal reforming of methane over lanthanum chromites modified with Ru and Sr*	CSIC	Hydrogen Power Theoretical and Engineering Solutions International Symposium	2015 September	Toledo (Spain)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
111	*Study of the effect of Re on the Activity and Stability of Pt/CeO2-TiO2 WGS Catalyst*	CSIC	Hydrogen POwer Theoretical and Engineering Solutions International Symposium	2015 September	Toledo (Spain)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
112	*An early transition of hydrogen-based transport in Europe by including the carbon price*	INERIS	Hydrogen : Road to the Green Future - Congress HYPOTHESIS XI	2015 September 6-9	Toledo (Spain)	Scientific community; Industry	200 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
113	*Poster - Gas Separation Membranes at TECNALIA – Mention of DEMCAMER project*	TECNALIA	Euromembrane 2015	2015, September 6-10	Aachen,(Germany)	Scientific community; Industry	800 Ca	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
114	*Poster - A density functional theory study on VNiTi alloys used in hydrogen separation*	TECNALIA	Euromembrane 2015	2015, September 6-10	Aachen,(Germany)	Scientific community; Industry	800 Ca	European Countries; China, South Korea; India; Iran; Israel;

	membranes							USA; etc.
115	*Presentation of DEMCAMER project*	TECNALIA	Hannover Trade Fair	2015	Hannover (Germany)	Scientific community; Industry	500 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
116	*Oral presentation - Membrane reactor with thin Pd-alloy supported membrane for syngas upgrading*	UNICAL	ECCE 10	September 27 – October 1, 2015	Nice (France)	Scientific community; Industry	1000 ca.	European Countries; China, South Korea; India; Iran; Israel; USA; etc.
117	PhD, Thesis of C. Günther	IKTS	Development of Sodalite Membranes for the Gas Separation in Industrial Conditions	2014	TU Dresden (Germany)	Scientific community; Industry		World wide
118	Thesis for Master of Industrial Sciences: Chemistry	VITO	Oxidative Coupling of Methane	2015 January	Faculty of Applied Engineering, Univers. of Antwerp, 2015	Scientific community; Industry		World wide
119	PhD Thesis of Ilaria Mirabelli	UNICAL	Analysis of Membrane Reactor Integration in Hydrogen Production Process	2015 February	The University of Calabria	Scientific community; Industry		World wide
120	Thesis for a PhD	VITO	Operando X-ray Chemical Imaging of Catalytic Systems	to be submitted in 2016	Department of Chemistry - University College London (UK)	Scientific community; Industry		World wide
121	Thesis for a PhD (Arash Helmi)	TUE	Micro-structured Membrane reactors for water gas shift (WGS) reaction	Drafting the thesis	Chemical Process Intensification (SPI). TUE	Scientific community; Industry		World wide
122	Thesis for a PhD (Ekain Fernández)	TUE	Development of Pd-based membranes and their integration into WGS membrane reactors	Drafting the thesis	Chemical Process Intensification (SPI). TUE / TECNALIA	Scientific community; Industry		World wide

---

[i] Process Intensification, David Reay, Colin Ramshaw, Adam Harvey, Elsevier, 2008.

[ii] Reay, D.A. (2007). Plenary paper, Proceedings of Pres 07, Ischia, June.

[iii] G. Barbieri, A. Brunetti, G. Tricoli, E. Drioli, , Journal of Power Sources, Volume 182, Issue 1, 15 July 2008, Pages 160-167, ISSN 0378-7753, http://dx.doi.org/10.1016/j.jpowsour.2008.03.086.

[iv] HyWays project, funded by the European Commission under the Framework Program 6, contract N° 502596, http://www.hyways.de

v "Hydrogen Generation Market by Geography, by mode of Generation & Delivery, by applications and by Technology - Global Trends & Forecasts to 2019" , Markets and Markets Analysis

[vi] http://www.world-petroleum.org (2015)

[vii] IEA 2007

[viii] IEA, 2010c

[ix] Shell International BV and Energy Balances of OECD and Non-OECD Countries©OECD/IEA 2010

[x] COM(2010) 2020 final: EUROPE 2020: A strategy for smart, sustainable and inclusive growth.

[xi] COM(2009) 279/4. "A sustainable future for transport: Towards an integrated, technology-led and user friendly system"

[xii] Biofuels Tecnhology Roadmap. IEA (2011)

[xiii] http://breakingenergy.com/2013/12/09/shell-gtl-decision-another-black-eye-for-louisiana-energy-future/

[xiv] http://www.eia.gov/todayinenergy/detail.cfm?id=15071 (february 2014)

[xv] http://www.pewclimate.org/docUploads/10-50_Ogden.pdf

[xvi] http://www.iea.org/Textbase/work/2005/renewable/Session3/Hydrogen_IA_T_R_final.pdf

[xvii] http://www.hydrogen.energy.gov/pdfs/5013_h2_cost_goal.pdf

[xviii] Major Chemicals Market Outlook -April 2008

[xix] http://www.icis.com/V2/chemicals/9075776/ethylene/pricing.html

[xx] Hugill et al., Applied Thermal Engineering, 25, 1259-1271, 2005 ; IRR = internal rate of return

[xxi] http://www.eia.doe.gov/oiaf/ieo/liquid_fuels.html

[xxii] http://www.oecd.org/dataoecd/13/42/36746373.pdf