FERRET

A FLEXIBLE NATURAL GAS MEMBRANE REFORMER FOR M-CHP APPLICATIONS

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Start date of project: 01/04/2014 **Duration: 3 years**

WP1 – Project Management

D1.4
18 Months interim activity report

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Dissemination Level		
PU	Public	
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	X
CON	Confidential, only for members of the Consortium	

(*) for generating such code please refer to the Quality Management Plan, also to be included in the header of the following pages

(**) indicate the acronym of the partner that prepared the document

Content

1. EXECUTIVE SUMMARY (3 pages max. all points)

Development of a catalyst stable to fluidization is one of the objectives of WP2. This was achieved by use of a strong stable support material that also wouldn't degrade the membranes developed in WP3.

The catalyst has also to be stable to a varying natural gas feed ranging from higher ethane fractions to larger nitrogen fractions and almost pure methane. Additionally the catalyst has to produce enough hydrogen to meet the project objectives and maintain an equilibrium conversion of ~95% converted methane at 600 ^{o}C.

Finally catalyst has to be scalable from a lab based preparation to provide over 3 kg of catalyst for the FERRET reformer unit.

WP3 developed this Pd membranes and pore filled membranes for the lab scale reactor. The thin film membranes have characteristics that meet the FERRET targets. For the pore filled membranes still the selectivity is too low, mainly due to the low permeation flux. Thus the thin Pd membranes have been selected for the scale-up in the prototype. All membranes required for the prototype including spare membranes, have been produced and delivered to TUE for the sealing. After sealing these membranes will be delivered at HyGear for integration in the fluidized bed reactor.

WP4 concentrated on the integration of catalyst and membranes and the testing of the reactor at lab scale. The catalyst was tested from the very beginning together with the membranes to check if any interaction occurs. No interaction was found (i.e. the membrane flux does not decrease and the catalyst is not damaged). During last period (M10-M14) catalysts received from JM were characterized before and after some reactive test in presence of a Pd-Ag-Au membrane provided by Tecnalia.

The catalyst was integrated in a MR and some reactive experiments were carried out. SMR and ATR reactions were performed at 500 °C and 550 °C at different pressures and steam to carbon ratios. For ATR experiment O/C ratio was fixed to 0.25 (close to the real value for autothermal operation). The catalyst showed high methane conversion, close to the theoretical ones for both conventional reactor and membrane reactors.

No interaction between catalysts and membrane was found. However, the selectivity of membrane decrease dramatically while experiment was running, due to the nitrogen permeation was increasing. After the experiments, leakages from the membrane surface and the sealing were detected at 0.5 bar of pressure difference.

In WP5 the prototype reactor was designed based on the results of the catalyst behaviour and characteristics and the membrane behaviour. All material has been ordered while also membranes and catalyst are under preparation.

Concerning WP6, a m-CHP system model was developed by POLIMI and validated using experimental results from tests performed at HyGear. The results from this analysis were used as reference case within the project. The performance of FERRET unit will be compared to this reference system: 28% for the net electric efficiency and 86% for the total efficiency of the CHP system. Furthermore, the natural gas compositions across Europe have been investigated and among the 37 different NG compositions available, 4 cases were selected as representative of the entire European situation.

Starting from the interaction between industrial partners and POLIMI, the input required for the modelling and assessment of the CHP system integrated with the fuel processor were defined. The layout of FERRET fuel cell CHP-system was identified: a good compromise between efficiency and membrane area occurs at 8 bar and 873 K with a net electric and total respectively higher than 41 % and 97%. In this particular case, a sweep gas is adopted in the membrane reactor to enhance hydrogen permeation.

The impact of NG composition on system design and performances was evaluated both at rated and partial load conditions. Results showed that the adoption of the most diluted natural gas (NL case) is suggested in order to guarantee a high efficiency at any NG composition.

The WP7 goals were about the dissemination of the achievements in FERRET project as well as the identification of results to be exploited. In order to achieve these goals, significant effort has been made by the consortium. A first document summarizing the plan for use and dissemination of the project result has been composed after agreement with all partners of the FERRET project. The document has been submitted with the deliverable D7.9. The dissemination is proceeding as planned. It is worth noting that among the different dissemination events, FERRET results were presented in the International Conference on Catalysis in Membrane Reactors, where the work on pore-filled membranes has been granted the Best Poster presentation prize. Additionally, two papers are under review in the International Journal of Hydrogen Energy. One paper is a collaboration between TECNALIA and TUE and a second one is collaboration between TUE and POLIMI, which also shows the good collaboration between partners of the project.

1.1. Description of the deliverable content and purpose

This deliverable reports the non-confidential information related to the first 18 months of the FERRET project.

1.2. Brief description of the state of the art and the innovation brought

N/A

1.3. Deviation from objectives

The deliverable was submitted after the periodic report has been submitted to the JU.

1.4. If relevant: corrective actions

N/A

1.5. If relevant: Intellectual property rights

N/A

2. WP1

2.1. WP1 - General objective

The objective of WP1 are the financial and technical coordination of the project.

2.1.1. Progress in the first 18 Months

Main activities during the present period were the establishment of management bodies and quality process to ensure an efficient coordination of the project. During the present period the following activities were developed:

- Overall administrative, contractual and financial management of the period (i.e. quality management plan, templates, financial follow up, submitting official reporting and amendment request to the EC)
- Management of Steering Committee meetings (i.e.; minutes…).
- Set-up of the internal communication tool and regular update of the information in the private consortium website.

The following activities were carried out by TUE during the period:

Task 1.1: Overall administrative, contractual and financial reporting [TUE] – Duration M1 – M36

The Project Coordinator (TUE) has been the official intermediary between the beneficiaries and the FCH JU. The Project Coordinator is also chairing the Steering Committee meetings and carried out the contractual tasks related to the implementation of the FCH JU contract and the project. In this sense he has carried out the following activities:

- Submitting official deliveries (see chapter “4.1 Deliverables”) and one amendment requests to the FCH JU,
- Managing the delivery and the follow-up of administrative documents,
- Managing the changes in the grant agreement (with Steering Committee approval).
- Being a permanent contact point for all the partners regarding their participation in the project,
- Preparing the official meetings and writing minutes.
- Following-up of actions and decisions,
- Creating common procedures and working and reporting tools for the project including different templates for administrative, technical and financial follow up (i.e., Minutes of Meeting; Invitation to Meeting, Working Document not related to the deliverables, Deliverable, Intermediate Progress Report, Resources follow up, Presentation,..).
- Validating the Steering Committee representatives and Work Package Leaders Committee representatives and updating the contacts in the committees and consortium.
- Following and updating the project indicators (Gantt chart, man power matrix, deliverables list).

1. Problems which have occurred and how they were solved or envisaged solutions

There were no problems to be solved during this period. The only issue was related to the legal status of one Partner. One amendment requests was submitted to the FCH JU on June 16th 2015. Main changes addresses in the amendment where:

- Adding HyGear Technology and Services B.V. and HyGear Fuel Cell Systems B.V. as third parties to HYG.
- Modification in Annex 1 according to the previous request.
- Change the date of two deliverables as for an error were too early in the original version of the DoW

2. Changes in the consortium

There were no changes in the consortium:

3. Any changes to the legal status of any of the beneficiaries

There are not changes in the legal status of any beneficiary during the period.

4. Other coordination activities

FERRET has also contacted other projects working in related R&D field. Main contact has been carried out with other FCH JU / FP7 project. Some of the project/consortia contacted are detailed hereafter:

- DEMCAMER - Design and Manufacturing of Catalytic Membrane Reactors by developing new nano-architectured catalytic and selective membrane materials (FP7, Grant Agreement nº: NMP3-LA-2011-262840).
- CARENA – Catalytic Membrane Reactors based on New materials for C1-C4 valorization (FP7, Grant Agreement nº: NMP3-LA-2011)
- ReforCELL - Advanced Multi-Fuel Reformer for Fuel CELL CHP Systems - ReforCELL (SP1-JTI-FCH.2010.3.3 - Grant agreement n°: 278997).
- CoMETHy - Compact Multifuel-Energy to Hydrogen converter – (FP7 - FCH JU, Grant agreement nº: 279075).
- Fluidcell – Advanced m-CHP fuel CELL system based on a novel bio-ethanol Fluidized bed membrane reformer – (FP7 – FCH JU, Grant agreement nº: 621196).

Apart from the collaboration with projects where TUE is partner, an intense collaboration was established and is continuing with the Coordinator and dissemination manager of Carena, Arend de Groot and Gilbert Rios, respectively.

Task 1.2: Partners meetings [TUE,** all**] – Duration M1-M36

Three main different regular (every 6 months) physical meetings are originally planned besides the individual internal technical work packages meetings: the Steering Committee, the Work Package Leaders Committee and the consortium meetings. These meetings are scheduled at the same time to decrease the number of travels. On the other side, the Steering Committee meetings were only convene when it was necessary. It was not necessary to have them during this period. The following meetings were carried out during the present period:

Table 1. List of physical Work Package Leaders Committee meetings during the 1st period of the project.

Meeting	Date	Venue

M6	16 September 2014	Johnson Matthey, Reading (UK)
M12	8 April 2015	TECNALIA, San Sebastian (SPAIN)
M18 (*)	14 September 2015	POLIMI, Milan (Italy)

(*) Follwing the discussion in the consortium meeting it was not necessary to have an specific WPL Committee meeting.

In any case, the Steering Committee could be convened for discussion / voting any time both physically or by telephone / e-mail.

In addition, the following physical Consortium meetings were organised:

Table 2. List of physical Consortium meetings during the 1st period of the project.

Meeting	Date	Venue
Kick-off	14 April 2014	TU/e, Eindhoven (The Netherlands)
M6	16 September 2014	Johnson Matthey, Reading (UK)
M12	8 April 2015	TECNALIA, San Sebastian (SPAIN)
M18	14 September 2015	POLIMI, Milan (Italy)

Additional, TUE organized interim 3 months telephone conferences to discuss the status of each WP between the members of each WP. Finally, monthly reports were asked to each WP leader to follow the progress of each WP in more detail and act faster in case of problems/changes.

Task 1.3: Internal Communication [TUE] – Duration M1 – M36

The internal communication has been accomplished with different channels. Firstly a private section of the website (www.Ferret-H2.eu) has been used to store and exchange deliverables, minutes, documents. The website is maintained on a Dutch server. TUE has also the possibility to use, and grant access to the partners, a FileSender (filesender.serf.nl) with which big files such as videos/data files can be exchanged between partners.

A mailing list of the most relevant contacts has been established and periodic e-mails are sent to the whole list to update on the status of the project.

3. WP2

3.1. WP2 - General objective

WP2 of the FERRET project involves developing fluidisable autothermal reforming catalysts tolerant to a range of natural gas compositions suitable for use in a membrane reforming reactor, catalyst testing in fluidised beds and membrane reforming reactors and scale up of catalyst production to provide suitable quantities of material for the CHP system. In WP2, catalyst development activities are carried out by Johnson Matthey including catalyst preparation, testing and characterisation. Following initial screening the most promising catalyst formulations are prepared at a larger scale and sent to TU/e for testing in a fluidized bed reactor and in conjunction with a membrane.

3.1.1. Progress in the first 18 Months

Task 2.1 Catalyst Preparation [JM] Duration: M1-18

Catalyst preparation for the project began with synthesis of catalysts on zirconia support materials due to previous problems in the Reforcell project. Catalysts exhibited inadequate stability and activity for the project and production of zirconia materials were stopped at M8.

Alumina support materials were used from M8 onwards and exhibited significantly improved activity and stability compared to previously tested materials. These materials were used to form the final FERRET catalyst for the pilot testing unit.

Task 2.1 has achieved completion and has been documented in D2.1 and D2.2.

Task 2.2 Catalyst testing [JM, TUE] Duration: M1-18

Catalyst testing for the project was undertaken on a fixed bed catalyst rig at JM testing the activity of the catalyst under a simulated natural gas, steam and air feed. The catalysts were tested across a range of temperatures from 500 ^{o}C to 600 ^{o}C and natural gas compositions, as outlined in WP6, to investigate the methane conversion and hydrogen production of the catalyst.

Long term testing (300+ hours) has been conducted to investigate the deactivation of the catalyst when exposed to reaction conditions. Catalysts show initial deactivation that can be attributed to thermal sintering of the catalyst support material.

Analysis of aged catalysts, including a sample tested at TUE under fluidization conditions, have been conducted and this confirms the above conclusion through BET and XRD measurements.

Task 2.2 has achieved completion and has been documented in D2.1 and D2.2.

Task 2.3 Catalyst manufacture and scale-up [JM] Duration: M12-18

Catalyst scale-up has shown no problems with batch sizing and catalyst is being prepared to dispatch to HyGear at M19.

Task 2.3 will have achieved completion in M19 and is documented in D2.3.

4. WP3

4.1. WP3 - General objective

The main objective of this WP is the development of Pd based tubular membranes, for application in natural gas autothermal reforming catalytic membrane reactors, with improved flux and selectivity, low cost, high temperature (550-650 ºC) and sulphur resistance and durability under conditions of reaction in a fluidization regime. Two types of Pd based membranes are considered: thin film and pore filled Pdbased membranes: a) Conventional supported Pd based membranes: The dense selective membrane will be deposited using the procedure developed at Tecnalia for the ReforCELL and DEMCAMER EU projects. In FERRET, the permeation characteristics of the membranes will be improved, the process of fabrication and post treatment will be scaled up. b) Pore-filled membranes: In this configuration, Pd is deposited inside the nano-porous of a ceramic below a protective porous ceramic layer. The PF membranes are more resistant to fluidized bed reaction conditions and will be for the first time used in fluidized bed reactors. The membrane performances will be first validated in lab-scale autothermal reforming catalytic membrane reactor in WP4 and then, the optimal membranes, will be used in the pilot prototypes in WP5.

4.1.1. Progress in the first 18 Months

Task 3.1: Preparation and characterization of tubular porous ceramic and metallic supports [TECNALIA] – Duration M1-M24

In order to prepare suitable thin membranes (thickness < 5µm, high enough H_2 permeance and H_2/N_2 selectivity, stable at reformer reaction temperatures (~ 600 °C)), the Pd-Ag alloy selective layer should be deposited onto supports with low roughness having small pores (<200 nm) with uniform pore size distributions. Besides, the selective layer should not react with the support. Asymmetric ceramic supports having ZrO2 100 nm pore size on the surface from Rauschert Kloster Veilsdorf have these characteristics. These supports were selected as the ceramic support for FERRET. Ceramic tubular porous supports (10/7 mm o.d./i.d., 25 cm long) are prepared for the further deposition of the selective layers. The final membrane length is around 23 cm long. 50% longer than the target set in the project.

Within ReforCELL project (FCH JU granted project), TECNALIA prepared 4-5 microns thick Pd-Ag membranes supported on ceramic coated metallic porous supports (13 - 15 cm long membranes). The characterisation of these membranes has been carried out in parallel to the 1st FERRET period. The membranes have shown extremely high ideal H_2/N_2 selectivity but moderate permeation when compared to the ceramic supported membranes permeation developed by TECNALIA (Table 3) but still higher than commercial self-supported membranes.

Table 3. Hydrogen permeation properties of thin Pd based membranes developed at TECNALIA.

Membrane	Support	Thickness (µm)	Technique	Temp °C	Calculated Permeance $x10^{-7}$ mol $m^{-2}s^{-1}Pa^{-1}$ at 1 atm	Selectivity H_2/N_2
Pd_{85}-Ag_{15}	α-Al_2O_3	4	ELP	400	42	20,000
Pd_{85}-Ag_{15}	α-Al_2O_3	3.2	ELP	400	31	8,000-10,000
Pd_{85}-Ag_{15}	ZrO_2	4	ELP	550 600	46 52	6,000 – 9,000
Pd_{85}-Ag_{15}	Metallic	4-5	ELP	500-600 *	10	>200,000
Pd_{85}-Ag_{15}	Metallic	4-5	ELP	400 **	9	>150,000

* Test carried out at different temperatures. Test duration: 800h. Membrane not stable when T >550 ºC.
** Test duration > 1,200 h

Task 3.2: Preparation of conventional high temperature Pd-based membranes by PVD-Magnetron Sputtering [TECNALIA] – Duration M1-M6

The work during this period has been focussed on identifying the higher length of the membrane that could be coated in the PVD-system with uniform thickness (deviation lower than 5% or 10% in the thickness). The PVD-MS equipment can work with four different cathodes and up to 5 five gases. For the study, one and two cathodes were placed in different levels on one side. In this occasions Al targets were used as there are cheaper than the Pd / Pd-Ag targets. The profile (differences in the thickness regarding one position) will be the same despite depositing different elements. The thickness profiles obtained onto Ø10 mm glass rods with the different set ups: 1 target, 2 targets overlapping 50 mm, 2 targets separated by 30 mm and 2 targets separated by 65 mm are show in Figure 1. Central thickness of the profiles has been set at 1000 nm for comparative purposes. Depending on the central thickness of the selective layer as well as the maximum deviation allowed on the thickness we can identify the maximum length that can be coated. It is clear that the 23 cm length membranes can be coated with a deviation lower than 5%. When having a deviation of 10% and 1 microns thick average thickness, 30 cm long membranes can be coated.

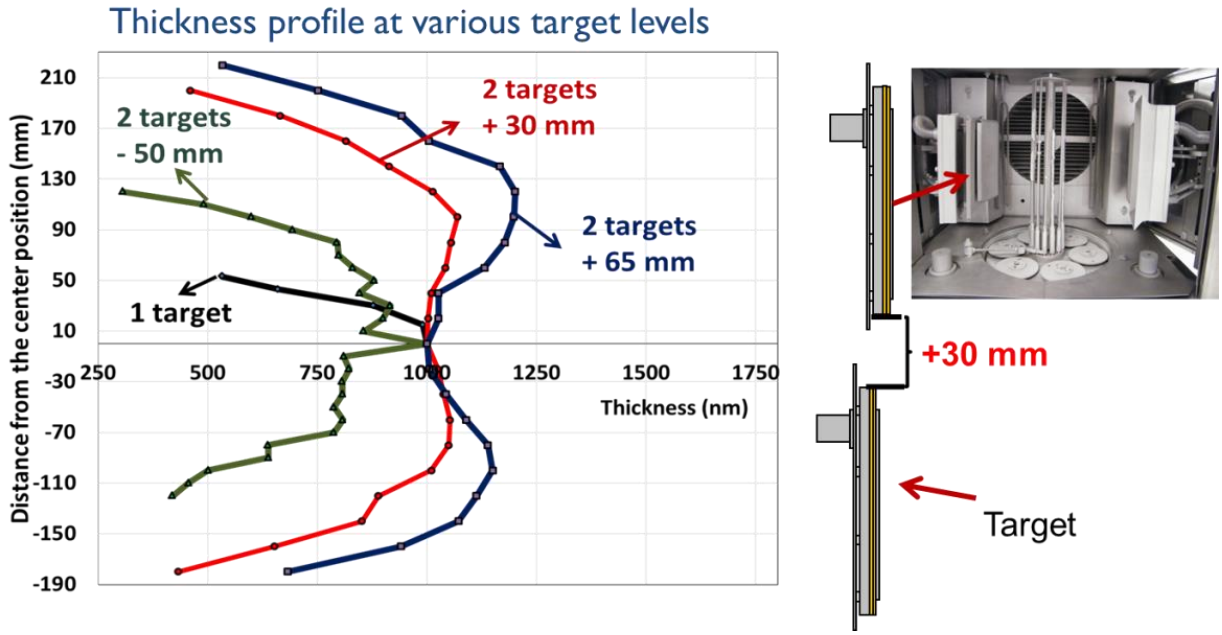

Figure 1. Thickness profile study on the PVD-MS. Central thickness of the profiles has been set at 1000 nm for comparative purposes.

Electroless plating (ELP) deposition. In addition to the Pd-Ag membranes developed for the pilot prototype, Pd-Ag-Au membranes have been prepared in two step process: Pd-Ag simultaneous electroless plating followed by Au electroless plating (see D3.1 and D3.3). Besides, seven further Pd-Ag membranes have been also prepared in the period and they are being used for developing further Pd-Ag-Au membranes with different Au content (see D3.4). On the other side, Pd-Ag-Ru and Pd-Ru membranes have been also prepared by simultaneous electroless plating deposition (see D3.4).

The H_2 and N_2 permeation properties of the E251 (Pd78-Ag10.6Au10.4) membrane tested at 550 °C and 1 bar of pressure difference are shown in Figure 2. At the beginning of the experiment, H_2 permeation increases sharply but after 300 minutes the permeation is almost constant. The permeation is close to 1.8×10^{-6} mol $m^{-2}s^{-1}Pa^{-1}$ after 50 h test with a H_2/N_2 selectivity of 1600 end of the test (50 h). The H_2 is somehow low comparing to Pd-Ag probably to the presence of Au. The effect of the Au content on the permeation properties of Pd-Ag-Au membranes will be studied in the following months.

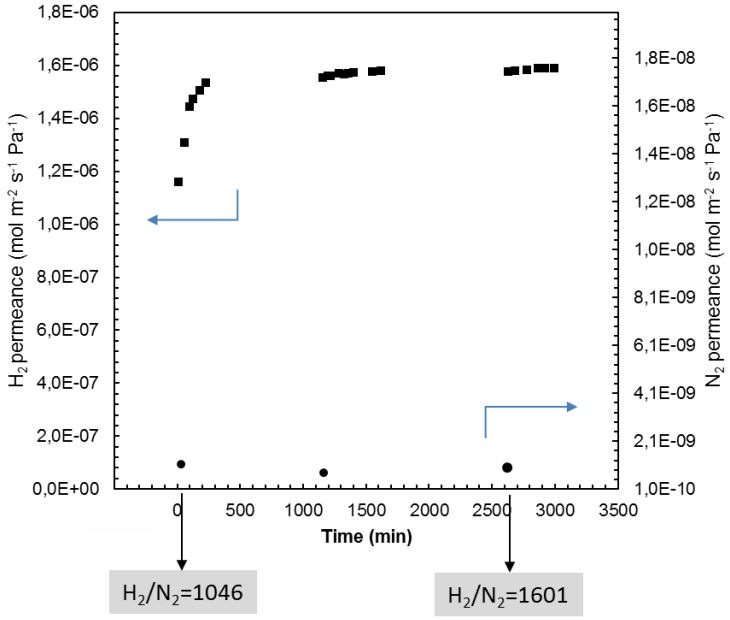

Figure 2. H_2 and N_2 permeances of E251 membrane (Pd78-Ag10.6Au10.4) in function of time at 550 °C and 1 bar of pressure difference.

Task 3.3: Development of a system for simultaneous healing of 6 Pd based membranes [TECNALIA] – Duration M6-M18

This activity has been postponed.

Task 3.4: Development of high temperature pore-filled Pd-based membranes [TECNALIA] – Duration M1-M18

First studies for the development of Pd-based pore-filled membranes using different YSZ-YAl_2O_3 mesoporous layers (YSZ content ≥ 50%) have been carried during this period. First approach has been the development of a suitable YSZ mesoporous layer (i.e. thickness, porous, stability) onto ZrO_2 porous supports (3 nm and 110 nm) but they showed bad adherence. The second approach has been the development of YSZ - Y-Al_2O_3 mixtures onto α-Al_2O_3 porous supports (100 nm and/or 200 nm). However, it has not been possible to prepare thick (≈3-4 µm) pore filled membranes without cracks during the period. The best developed mesoporous layers (without cracks) have less than 2 µm (Table 4).

Table 4. Mesoporous layers onto 100 nm porous alumina.

Sample	PF-A54	PF-A51	PF-A64	PF-A99	PF-A113
Total ceramic in dipping solution (wt. %)	1.2	1.3	1.4	1.5	1.6
Composition of mesoporous layer	90% YSZ 10 %Y-Al_2O_3	80% YSZ 20 %Y-Al_2O_3	70% YSZ 30 %Y-Al_2O_3	60% YSZ 40 %Y-Al_2O_3	50% YSZ 50 %Y-Al_2O_3
Thickness (µm)	0.73	0.83	1.29	1.57	1.92

Besides, the Pd pore filled membranes developed using this type of mesoporous layers do not show high enough H_2 permeances and their H_2/N_2 perm-selectivity are too low (<100) (Table 5).

Table 5. N_2 and H_2 permeances of some pore-filled membranes and their ideal H_2/N_2 selectivity obtained at different temperatures.

Sample	T (ºC)	N_2 perm (ΔP=1 bar) (mol m^{-2} s^{-1} Pa^{-1})	H_2 perm (ΔP=1 bar) (mol m^{-2} s^{-1} Pa^{-1})	H_2/N_2
PF-A15	400	4.21×10^{-9}	8.30×10^{-8}	18
PF-A41	450	8.85×10^{-10}	7.85×10^{-8}	85
	400	9.72×10^{-10}	7.02×10^{-8}	68
	350	1.14×10^{-9}	7.20×10^{-8}	61
	500	1.38×10^{-9}	9.88×10^{-8}	72
	300	1.29×10^{-9}	4.35×10^{-8}	38
PF-A45	400	7.15×10^{-9}	1.95×10^{-7}	27
	400 (after air treat.)	4.81×10^{-9}	1.45×10^{-7}	30

PF-A15 and PF-A45 (60% YSZ) / From FluidCELL: PF-A41 (50% YSZ)

Task 3.6: Manufacturing of larger scale Pd based membranes (scale-up). [TECNALIA] – Duration M19-M24

All membranes for the prototype were delivered. The lengths of these membranes are around 23 cm long, 50% longer than the target set in the project. Details will be reported in D3.6.

5. WP4

5.1. WP4 - General objective

Characterization of catalysts (Rh-CeO2/Al2O3/ZrO2) before reactive test: XRD, BET, partize size and shape. • Minimum fluidization velocity was obtained experimentaly at different temperatures (from room temperatura to 400 ºC) • Single gas test of membrane before integration of catalysts. • Setup models for the membrane reactor.

5.1.1. Progress in the first 18 Months

Task 4.1 Integration of catalyst and membranes in lab scale MR [TUE, TECNALIA, JM] – Duration M8 – M19

This task tested separately the catalyst developed in WP2 and the membrane developed in WP3 and then integrated both in a MR to test possible interaction between the two.

The catalyst received by JM has been tested at TUE under fluidization conditions to evaluate the mechanical stability of the particles under cold fluidization (room temperature) and hot fluidization (200-400 °C) without reaction. Particle size distribution was analyzed (with laser diffraction method) for three different conditions:

- Fresh catalyst (as received, before sieving)
- Fresh catalysts (after sieving)
- After the fluidization test with N_2 from room temperature (cold fluidization) to 400 °C (hot fluidization) for 48 h

It was observed that even under high temperature operation in bubbling fluidization regime the particle size distribution of the material does not change. So no agglomeration neither sintering phenomena occur during the fluidization.

Preliminary tests on the membrane behavior were performed in a single tube fluidized bed membrane reactor. The Pd-Ag-Au membrane (E251) supported on ZrO_2 (110 nm pore size) was provided by Tecnalia with OD of 10.4 mm. Membrane was sealed at TUE following the procedure as described in [1]. Once sealed, the final length of the membrane was 47 mm.

First, some thermal cycles were performed to evaluate the N_2 leakage (principally due to the sealing) at 500 ºC and 550 ºC and the performance of the membrane in terms of H_2 permeation (400 - 500 ºC). Before integration of the catalyst, single gas tests (H_2 and N_2) of the membrane E-251 were performed at 400 ºC and 450 ºC. The H_2 permeance of the Pd-Ag-Au (~11,6% Ag & ~10,4 % Au) membrane are presented in Table 6. Those values are one order of magnitude below the target. Nitrogen permeance was measured applying vacuum at the inner part of the membrane and it was around 10^{-10} mol m^{-2} s^{-1} Pa^{-1}.

Table 6. Hydrogen permeance of membrane E-251 at 400 ºC and 450 ºC.

T(ºC)	H_2 permeance at 4 bar (mol m^{-2} s^{-1} Pa^{-1})
400	$2{,}68\times10^{-7}$
450	$3{,}41\times10^{-7}$

The explanation for this H_2 permeance could be that the gold is not well alloyed with Pd and Ag or the surface was not completely activated. For that reason the membrane was heat up to 550 ºC in order to improve the H_2 permeance. Hydrogen permeance at 1 bar of pressure drop increased from 1.16×10^{-6} to 1.6×10^{-6} mol m^{-2} s^{-1} Pa^{-1} after 2 days and reach to the steady state (see WP3). Moreover, the H_2/N_2 permselectivity was improved from ~1000 to ~1600 (note that the very low selectivity, compared to the target, is due to the very short membrane). During this test the measured nitrogen permeance does not change and it was $<1\times10^{-9}$ mol m^{-2} s^{-1} Pa^{-1}.

Once, the hydrogen permeance of the membrane was stable, the membrane reactor was filled with 200 g of JM's catalyst in order to cover the surface of the membrane.

The methane conversion decreases when pressure is increasing because of the unfavorable shift in the SMR equilibrium (Figure 3). However, when hydrogen is permeating through the membrane, the CH4 conversion for SMR and ATR is greatly especially at higher pressures, showing the benefits of hydrogen extraction. It can be observed that methane conversion is at least 10% higher in ATR that SMR. The maximum CH_4 conversion achieved at S/C=3 and 550 °C was at 2 bara under ATR (83.60%) witch is close to the desired value (target 82.44%). The methane conversions obtained experimentally are 1-2% higher that the theoretical equilibrium conversion. This is due to the deviation on the temperature in the reactor, which fluctuates around 1-3 °C compared to the set value (used in the calculations).

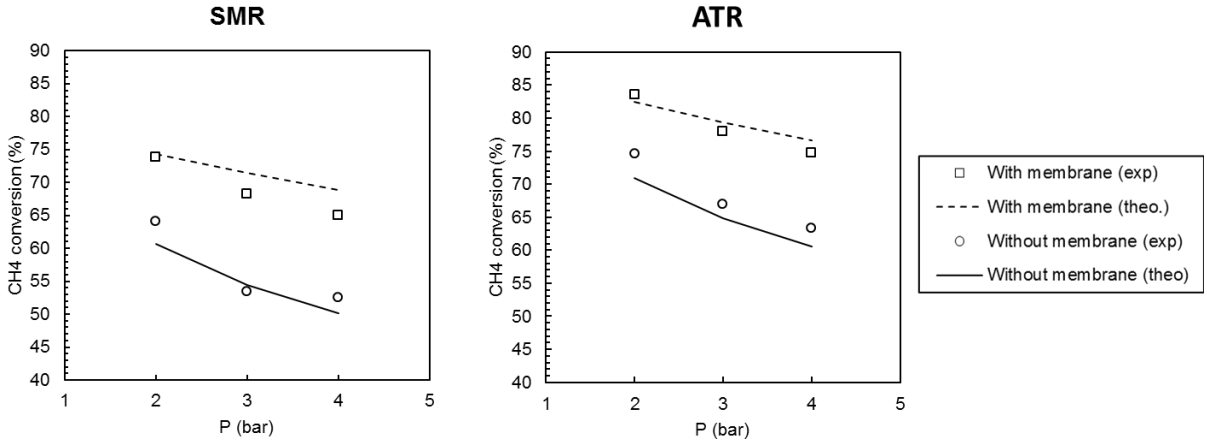

Figure 3. Methane conversion at different pressures of experiment carried out at 550°C and S/C=3. For ATR O/C=0.25

Due to higher H_2 extraction at higher pressures, separation factor (SF) and hydrogen recovery factor (HRF) increase as the pressure increases for both cases (SMR and ATR) as it can be observed in Figure 4.

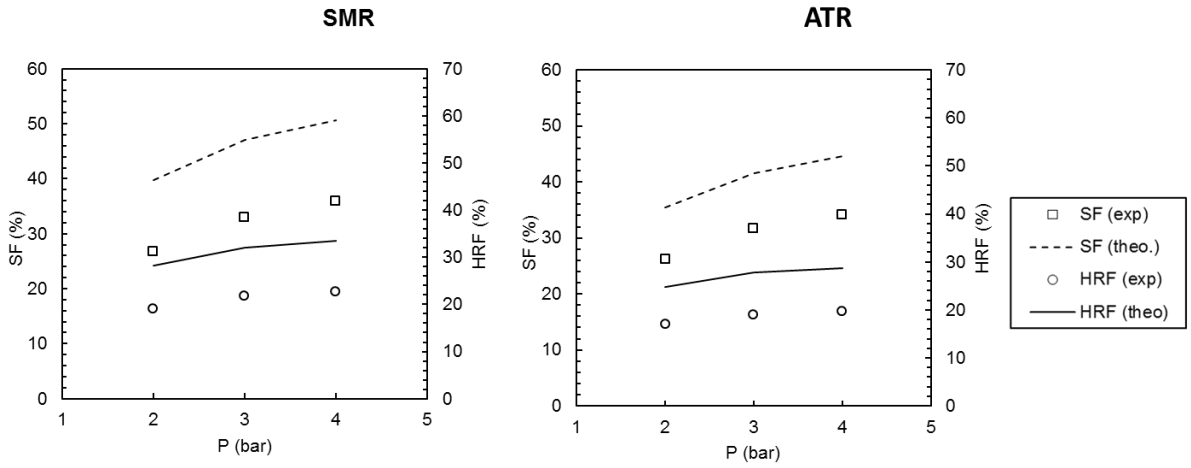

Figure 4. Separation Factor and Hydrogen Recovery Factor at different pressures of experiment carried out at 550 °C and S/C=3. For ATR O/C=0.25

Task 4.2 Setup, testing and validation of novel reactors at lab-scale [TUE, HYG] – Duration M12-M20

This task is still on going. The deliverable is foreseen at M20 so the results are not available for the first periodic report. However, it should be said that a reactor with 5 membranes has been sealed and is under testing at this moment with very good results.

Task 4.3 Modelling of the novel membrane reactor [TUE-POLIMI] – Duration M1-M24

This task is divided in two parts. A first comparison between membrane reactor configurations is carried out and afterwards a more detailed comparison is carried out. For the first part, D4.1 reports the modelling approach taken for this comparison.

The comparison has been carried out using both packed bed (PBR) and fluidized bed (FBR) configurations. In D4.1 the following plants will be compared:

Membrane assisted packed bed reactor using vacuum conditions (0.03 bar) at the permeate side without sweep gas and adiabatic conditions in order to take into account the effect of the temperature profile (referred as MA-PBR/adiabatic in Figure 5a).

Membrane assisted packed bed reactor using steam (1 bar) as sweep gas at the permeate side fed to the system co-currently respect to the fuel gasses (referred as MA-PBR/co-current in Figure 5b) and counter-currently (referred as MA-PBR/counter in Figure 5c).

Fluidized bed reactor using vacuum condition at the permeate side (0.03 bar) which is defined as FBR/vacuum (Figure 6).

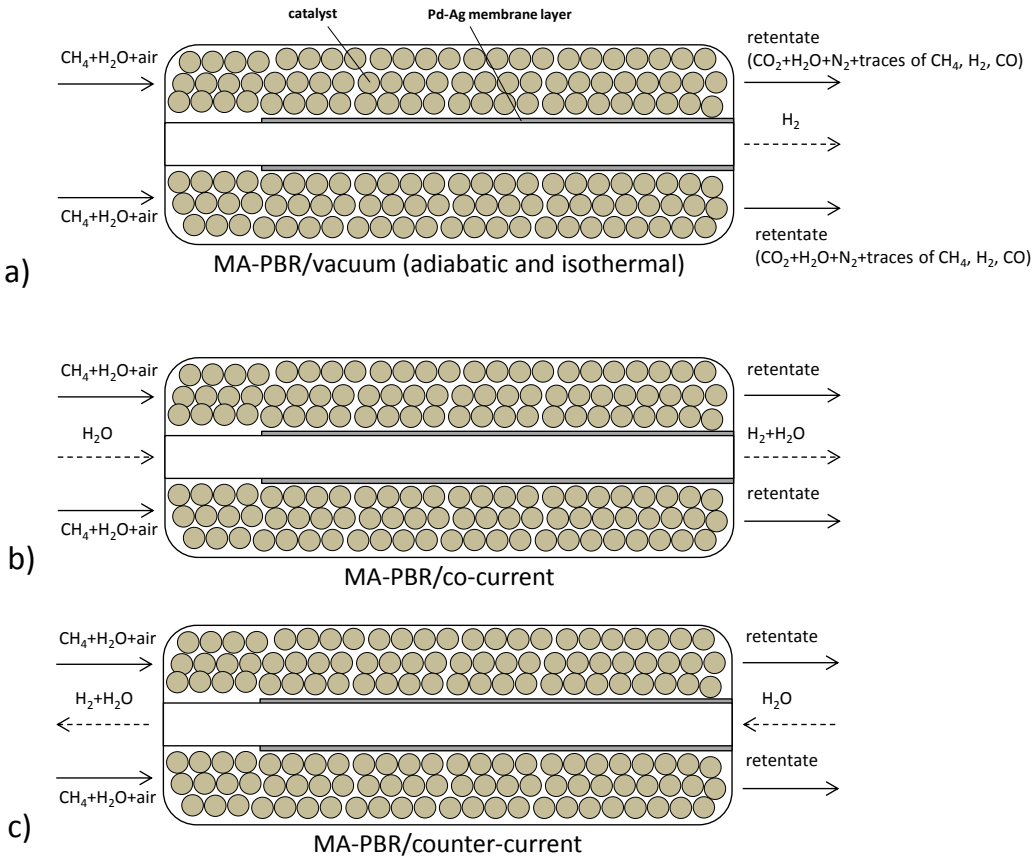

Figure 5. Membrane Assisted Packed Bed Reactor configurations.

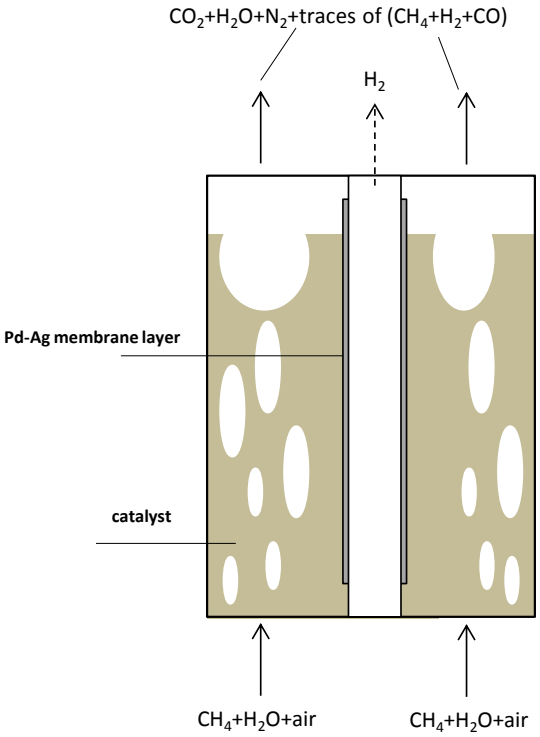

Figure 6. Membrane Assisted Fluidized Bed Reactor configuration.

The analyses are based on a dedicated kinetic model and permeation model for auto-thermal reforming reactions and Pd-based membranes, respectively.

The preliminary analysis of membrane reactor for auto-thermal reforming of methane to produce 5 Nm^3/h of H_2 has been carried in this deliverable. Two different reactor concepts have been compared: in the first case the membranes are located in a packed bed reactor which works with different conditions at the permeate side; in the second case, a fluidized bed reactor is used which is operated in bubbling regime. The results show that: i) for packed bed configuration, when the permeate side is at vacuum conditions, the H_2 flux is the highest, however this configuration is not interesting at industrial scale; ii) when using H_2O as sweep gas, the highest H_2 flux is achieved in counter-current feeding however the optimal conditions in terms of permeate pressure and/or sweep gas flowrate results from a techno-economic optimization; iii) in case of fluidized bed configuration, the H_2 flux is higher than in the case with packed bed reactor although the reactor requires a bigger diameter (50% bigger) to achieve the desired fluidization regime; iv) however a more refined model should be considered in order to validate the strategy adopted for the modelling (i.e. selection of the number of CSTRs for the different phases for fluidized bed and concentration polarization for the packed bed model) and the mass transfer model adopted in this study.

6. WP5

6.1. WP5 - General objective

WP5 takes over the development of the membrane reactor system from design up to validation before delivering to WP6 for final testing. As an overview the specific tasks include:

- Design of membrane reactor for pilot scale system

- Manufacturing of pilot scale reactor
- Design and assembly of test setup for membrane reactor
- Implementation of controls
- Functionality acceptance test
- Evaluation of performance of membrane reactor

6.1.1. Progress in the first 18 Months

The ATR membrane reactor was designed and constructed. The fuel processor is designed for a maximum capacity of 5 Nm^3/h of hydrogen with the nominal feed of natural gas which can modulate down to 30 %. Maximum operating temperature and pressure are of 600 °C and 7 bar_g. The reactor holds 15 tubular membranes with a total membrane area of 0.18 m^2 and is designed for flowing steam as sweep gas on the permeate side for enhancement of the driving force for permeation of hydrogen. The reactor will be tested as a stand-alone system for hydrogen production in WP5 and later integrated with the fuel cell in WP6.

7. WP6

7.1. WP6 - General objective

Integration and testing of the prototype against European NG compositions.

7.1.1. Progress in the first 18 Months

Task 6.1 Definition of the reference fuel cell CHP-system [POLIMI, HYG, ICI] Duration: M1 – M6.

European Natural Gas Composition

Among the 37 different NG compositions available, four cases were selected as reference for the FERRET project: UK3, IT3, NL (HyGear) and ES6. The four cases were selected as representative of the entire European situation: one average case and three extreme cases. The first case can be assumed as the European average composition in terms of CH_4 content and H_2 potential. IT3 and NL have respectively the maximum and the minimum value for the CH_4 concentration; in addition the third case is characterized by the lowest H_2 potential and the higher value of N_2. The last reference case ES6 was selected for both his high H_2 potential and LHV due to the large presence of hydrocarbons heavier than methane.

Table 7. FERRET Natural Gas Reference cases.

		NG type			
Species	**Unit**	**UK3**	**IT3**	**NL**	**ES6**
CO_2	**%mol**	0.865	0.029	0.89	0.000
N_2	**%mol**	2.375	0.296	14.4	0.690
CH_4	**%mol**	92.070	99.581	81.23	81.570
C_2H_6	**%mol**	3.405	0.056	2.85	13.380
C_3H_8	**%mol**	0.761	0.021	0.37	3.670
n-C_4H_{10}	**%mol**	0.177	0.002	0.08	0.400
i-C_4H_{10}	**%mol**	0.140	0.006	0.06	0.290
n-C_5H_{12}	**%mol**	0.048	0.000	0.02	0.000
i-C_5H_{12}	**%mol**	0.061	0.002	0.02	0.000
C_{6+}	**%mol**	0.090	0.007	0.08	0.000
SUM	**%mol**	99.992	100.000	100	100.000
LHV	**MJ/kg**	46.740	49.730	38.0	48.610
LHV	**MJ/mol**	0.819	0.801	0.71	0.939
H_2 potential	**mol H_2/mol NG**	4.07	3.992	3.523	4.656
x in CxHy	**-**	1.035	0.998	0.892	1.221

Reference Fuel Cell System

A system model derived from the layout of the existing fuel cell system placed at HyGear was developed in Aspen Plus. The process flow diagram of this unit is shown in Figure 7.

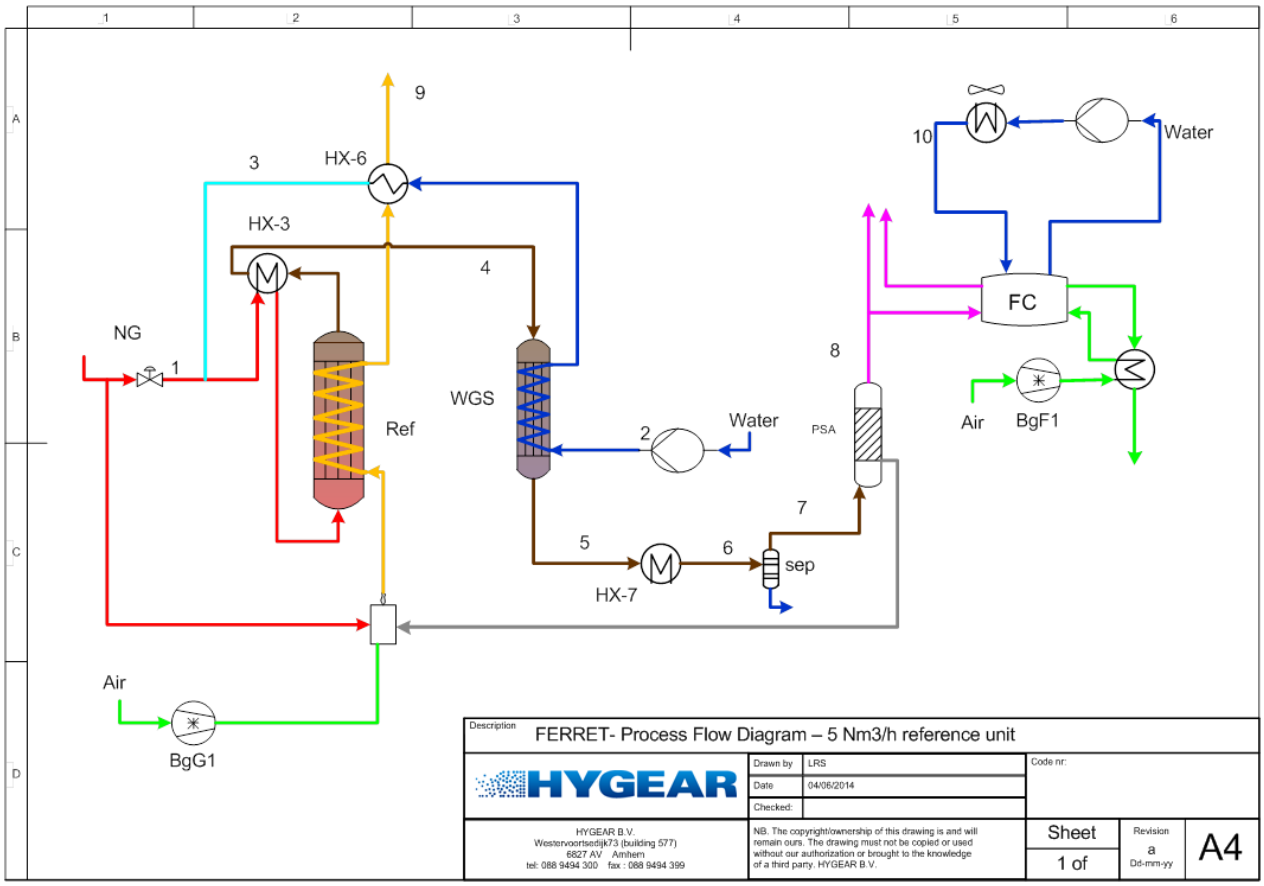

Figure 7. Process Flow Diagram of the reference system.

The reference unit was designed as a hydrogen generation system capable of reaching high level of purity required for a PEM fuel cell.

Task 6.2 Definition of a fuel cell CHP-system [POLIMI, HYG, ICI] Duration: M7 – M20

Several layouts and operating conditions for the FERRET unit have been investigated. The definition and optimization of the unit performances and layout have been carried out developing a model in Aspen Plus.
A good compromise between efficiency and membrane area occurs at 8 bar and 873 K for the sweep gas case with a net electric and total efficiencies respectively higher than 41 % and 97% (detail in D6.2).

Performances at partial load were also assessed. Main outcomes were: the peak efficiency occurs at 70-80% of the load, the vacuum pump lay-out is penalized both at design and rated loads and the differences in terms of net electric efficiency between different NG compositions evaluated are constant throughout the operating regime.

8. WP7

8.1. WP7 - General objective

The objective of the WP7 is to coordinate the dissemination and exploitation activities performed during the project. For the first 12 months of the FERRET project all three task were relevant.

8.1.1. Progress in the first 18 Months

Task 7.1: Dissemination follow-up [POLIMI, all partners] – Duration M1-M36

Different actions have been carried out to disseminate the goals and achievements of the project within the first 18 months.

Activities can be divided between more general actions to communicate the project achievements to a generic public and activities dedicated to the scientific community focusing on one particular aspect of the project. General actions were: creation of a web-page, preparation of a Public presentation and leaflet, submission of a biannual newsletter to a selected mailing list.

As for scientific audience, partners of the project attended to workshop and conferences with specific presentations. Two papers were submitted for publication to scientific journals, but they have not been published yet-

Task 7.2: Exploitation strategy implementation [HYGEAR, all partners] – Duration M1 – M36

An exploitation plan is developed in a two stage process which begins with the elaboration of FERRET industrial roadmap and is completed with a final report on the exploitation plans relevant to fluidized bed membrane reactor. The former stands on information brought by the PUDF and expands over the forecast of deployment of the technology from lab to market. The deliverable is planned for M24 from annex 1. The latter will focus on the exploitation of the fuel processor and its developed technologies (i.e. membranes and catalyst). A first version of the PUDF is developed during the first reporting period. The elaboration of data from all partners took longer than planned and the deliverable will be submitted 2 months delayed. This delay does not place risks on the development of the final version.

Task 7.3: Organization of dissemination / exploitation project workshops [TUE, all partners] - Duration M1 – M36

A mid-term exploitation workshop was held at the premises of Tecnalia (after the second progress meeting). The workshop was carried out in order to identify non-technical factors, which could represent a risk that future results of the project would remain unexploited and to achieve a common understanding about IPRs and exploitation.

The workshop included sessions for addressing the following areas:
1. Identification of exploitable results
2. Intellectual Property Rights and Exploitable Claims situation
3. Risk assessment and management

The results from the analysis are reported in the first version of Plan for Use and Dissemination of Foreground (PUDF) (see D7.9).

9. ANNEXES