



Joint Workshop on
Scale-up of Pd Membrane Technology
From Fundamental Understanding to Pilot Demonstration

November 20 & 21, 2014. The Netherlands.



Venue: ECN, Westerduinweg 3, 1755 LE Petten,
The Netherlands



Workshop objectives, summary and outcomes

Thanks to their outstanding hydrogen selectivity, palladium membranes have attracted extensive R&D interest in the 21st century with promising “breakthrough” applications for hydrogen power, refining and petrochemicals, hydrogen vehicles and many more. The workshop is the follow-up of the first “Pd-membrane Scale-Up” workshop (Roma, Italy, November 2012), a unique knowledge-sharing experience for both the EU-funded organizing projects and all participants. This experience has strengthened the belief that there is a need and a ground for the second workshop, where the whole Pd-membrane R&D spectrum “From Fundamental Understanding to Pilot Demonstration” has been further explored together by representatives of academia, research institutions and industrial stakeholders.

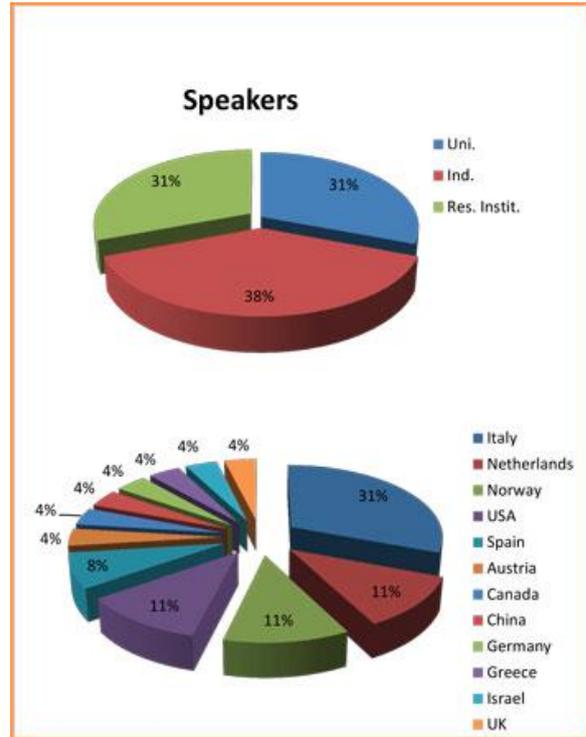
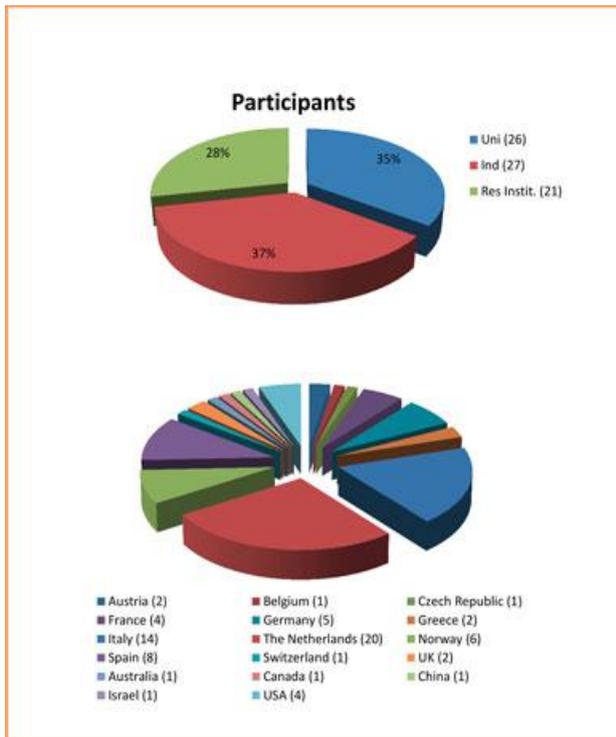
CARENA, CoMETHy, ReforCELL and DEMCAMER are four research projects funded by the European Commission through FP7. Although the projects were originated from two different funding priorities, CARENA and DEMCAMER under the NMP and CoMETHy and ReforCELL under the FCH JU priority, the four projects have found commonality and synergy in their research objectives related with the development of palladium membranes for hydrogen production. Due to such technology synergy, the four projects have joined forces to organize a workshop together, focusing on “Scale up of palladium membrane technology: From fundamental understanding to pilot demonstration”.

The two-day workshop was organized at the Energy Research Centre of the Netherlands ECN, Petten, The Netherlands on 20-21st of November 2014, including presentations, interactive discussions and a visit to the ECN membrane test facilities and biomass gasification and gas clean-up facilities.

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. In addition to presentations from members of the four organizing projects, there was also a significant amount of presentations from the representatives from industry. The presentations covered a good breadth of topics that are critical for palladium membrane technology scale-up: from the fundamentals of palladium membranes, hydrogen transport mechanisms and long term behavior, to various concepts of membrane module design and system integration and from lab-scale testing to industrial pilot plant operational insights.

Both days of presentations were finalized with an interactive discussion session on the relevant topics of the presentation sessions of the day. The package of presentations together with the interactive discussion gave a very clear picture of the status of palladium membrane technology and the critical issues to be addressed in the near future.

In this document, a short overview of the sessions, and abstract of the presentations are given.



Session 1: Fundamental Aspects of Membrane Technology

The first session of the workshop focused on fundamental aspects related to the Pd membrane technology. At first Prof. Venvik (NTNU) presented fundamental phenomena affecting the performance of thin Pd-Ag membranes, like the effect of various heat treatments on H₂ flux, and the effect of membrane thickness on the H₂ solubility and diffusivity, respectively. Subsequently, Dr. Caravella (UNICAL) discussed the coupled influence of surface and concentration polarization effects on membrane performance. Operation of the current state-of-the-art thin Pd-alloy membranes has made external mass transfer limitations, or concentration polarization, progressively more influencing.

The 2nd part of the session focused on membrane stability and robustness, and discussed the impact of contaminants and membrane long-term stability under realistic operating conditions. Dr. Sanchez (CIEMAT) and Dr. Peters (SINTEF) presented experimental results on the impact of syngas components - CO₂, H₂O, and CO - on the H₂ permeance, and the performance of Pd-Ag alloy membrane films under exposure of trace amount of H₂S, respectively. The long-term stability over periods exceeding 100 days was presented by Dr. Goldbach (DICP) for WGS conditions, and by Dr. van Berkel (ECN) for operation under methane steam reforming conditions. Possible degradation mechanisms were discussed. On behalf of Prof. Way (CSM) Dr. Lewis (Pall Corporation) presented possible means to increase the high temperature stability of Pd alloy composite membranes, and the application of these membranes in an integrated steam methane reforming membrane reactor.

Session 2: Manufacturing and Scale-up Challenges

After the comprehensive overview of fundamental aspects of Pd membrane technology discussed in session 1, session 2 was mainly focused on Pd membrane production and scale-up challenges, including manufacturing, design and construction.

Initially, Processi Innovativi presented their R&D results on the optimization of porous metal support to enhance the Pd-alloy deposition, obtained in CoMETHy project. Processi Innovativi emphasized that the quality of the metal support, particularly the surface roughness, is crucial to obtain a satisfactory (defect-free) deposition of either the ceramic inter-metallic barrier layer and the thin film Pd-alloy. It was showed that samples with satisfactory support smoothness have been developed. Another important issue is the welding between the porous and the solid supports. Some open issues are still pending to obtain Pd-alloy metal-supported membranes with the desired quality, and optimization work is in progress. Tecnalía presented several developed configurations and preparation methods for Pd-based membranes. In this overview different supports, either porous ceramic and metallic supports, have been considered as well as different preparation methods and applications.

Another important topic is the possibility related to the Pd recovery after membrane replacement, discussed by Ecorecycling. It was emphasized that Pd recycling is a fundamental aspect to be considered in membrane/plant design and operation, as well as to make Life Cycle Assessment of the technology.



Another important topic considered in session 2 is dealing with membrane reactor and plant design and optimization. The ITM-CNR (in cooperation with UNICAL), the Eindhoven University of Technology and Technion presented their results obtained in different projects (DEMCAMER, CoMETHy, CARENA, RE4CELL) dealing with the integration of Pd membranes in chemical plants. Concentration polarization and inhibition phenomena should be considered in reactor design, modelling, and simulation. It was also outlined the importance of the optimization of the whole process with respect to the energy efficiency, with a proper tuning of the design and operating parameters (e.g. the sweep gas flow rate for permeate hydrogen extraction). To this regard, different plant schemes and examples have been presented. The ITM-CNR emphasized the advantages of integrating membrane reactors in new plant schemes to enhance process integration, optimization and intensification (and compactness). The TU/E presented an innovative fluidized bed membrane reactor integrated in a process scheme designed to achieve high energy conversion efficiency with simultaneous CO₂ capture. Technion also presented its experimental results obtained in CoMETHy, where the same integrated membrane reactor used for methane steam reformer has been successfully applied to ethanol steam reforming, without any evidence of performance loss after several months of operation.

Session 3: Towards Industrial Applications

The session focused the main aspects relevant to the application of the membrane in the industry, linked either to the development of the membrane either to their integration in process scheme with techno-economic analysis.

Examples of palladium membranes and membrane reactors were given by Pall Corporation, Johnson Matthey, and NORAM Engineering and Constructors. The durability and stability of the membrane as well as the chemical resistance were strongly addressed, and still considered the possibility to alloy Pd to improve for instance the resistance to carbon and sulphur. Up to 1 m long membranes are currently prepared in Johnson Matthey, the main application of which is downstream to a coal gasifier. PdAg membranes are currently under study also in Noram Engineering, as well as their application in autothermal fluidized bed reactors. The fluidized bed reactors are able to work and operate in a stable and reliable manner, even if some technical challenge as membrane stability over months of operation still remain.

Methane steam reforming tests with membrane integrated reactors were performed at CERTH in the framework of CoMETHy project, evidenced very good results both in terms of catalyst deactivation absence both in terms of membrane stability, even if a loss of selectivity was observed. A series of simulation studies were also presented. The membrane application in water gas shift or autothermal reforming membrane reactors, as well as their integration in micro combined heat and power systems, were considered.

Session 4: Alternative Applications

Session 4 was focused on the application of membrane reactors in dehydrogenation reactions. After an overview and an update on the application of membrane reactors and micro membrane reactors in some dehydrogenation reactions like, methane steam reforming, propane dehydrogenation etc, presented by Dr. Dittmeyer, the investigation of the membranes and membrane reactors behavior in dehydrogenation reactions has been presented, focusing particular attention on the novel process schemes design of integrated systems where the core is represented by Pd-based membrane reactors.

Interactive discussion day 1 and day 2

The general theme of the interactive discussion was defined as “Research as usual and die or recognize fundamental shortcomings and live!”. The main background of this rather provocative statement is to come to a clearer view on the R&D requirements in order to make Pd-membrane technology a commercial success. Although it is realized that different stakeholders have different development agendas the current workshop was considered to be a good opportunity to get the general development problems or hurdles addressed. Ideally, the discussion should lead to a consensus on the directions towards solutions within the Pd-membrane technology development community. The interactive discussion on the first day concerned the critical hurdles in the Pd-membrane development where most emphasis was on membrane robustness. It was acknowledged that the importance of “keeping high H₂-selectivity over Pd-layer during long term operation” is underlined but the selectivity target has to be realistic and not better than required for a certain application. It was emphasized that the current understanding of the membrane long term behaviour still requires further fundamental R&D on long term behaviour and degradation mechanism of palladium membranes. Therefore a strong collaboration between University and Industry is required.

The interactive discussion of the second day was on critical hurdles in the application of the Pd-membranes with emphasis on the required and expected cost of the membrane and the expected maturity of the Pd-membrane technology over 10 years. It was concluded that it is not only about membrane cost but that the total module cost is of importance. In general there is confidence that cost reduction will be realised in the coming years; the market is well identified, reflected by the attendance of industrial stakeholders during the workshop and scale-up should have a positive impact on cost reduction. Both the realisation of a cost reduction and the increase in maturity of the technology requires the demonstration of the Pd-membrane technology on a pilot scale under realistic industrial conditions, preferably on an industrial site. For the near-term period, when the full market potential has not been reached yet, it would be realistic to focus on membrane module units with a price level of 10,000 €/m². The overall conclusion of the interactive session was that it is of utmost importance to strive for a successful pilot demonstration of the Pd-membrane technology in a relevant “realistic” operation environment. This will form a driver for further implementation of this technology in a variety of applications as addressed during the workshop. The market entry of the technology will take care of the further reduction of the cost.



Abstracts

Thursday 20 November

Project introduction of workshop partners

Introduction to CoMETHy: Compact multi-fuel-energy to hydrogen converter (Alberto Giaconia, ENEA, Italy).

Alberto Giaconia introduced the co-organizing project CoMETHy (Compact Multi-fuel-Energy To Hydrogen converter). This is a collaborative project, co-funded by the European Fuel Cells and Hydrogen Joint Technology Undertaking (FCH JU), coordinated by ENEA (Italy) and implemented by twelve organizations. In general, CoMETHy aims at the intensification of hydrogen production processes, developing an innovative compact and modular steam reformer to convert reformable fuels (methane, ethanol, etc.) to pure hydrogen, adaptable to several heat sources (solar, biomass, fossil, etc.), depending on the locally available energy mix.

Alberto Giaconia initially explained where CoMETHy is set in an energy policy aiming at fuel decarbonization. After, the technological approach behind CoMETHy is presented: the concept is based on the low-temperature steam reforming, where molten nitrates at temperatures below 550 °C are used as heat transfer fluid from the heat source (including solar energy) to the chemical plant exploiting Pd-based membranes for hydrogen separation. The development of this new process passes through a number of interconnected challenges: first, the basic materials and components have been identified, i.e. advanced low-temperature reforming catalysts and hydrogen separation membranes; second, the suitable membrane reactor concepts have been developed to best fit with the process powered by molten salts; third, experimental proof-of-concept is achieved at the prototype and pilot scale; finally, the best strategies to couple the steam reformer with the primary energy source (i.e. the CSP plant) are studied. Alberto Giaconia finally outlined the specific contribution of CoMETHy to the workshop, including four CoMETHy-related presentations discussing results obtained on membrane development, membrane reactor design and operation, process integration, and applications.

Introduction to ReforCELL: Advanced multi-fuel reformer for fuel CELL CHP systems (José Luis Viviente)

Distributed power generation *via* Micro Combined Heat and Power (m-CHP) systems, has been proven to overcome disadvantages of centralized plant since it can give savings in terms of Primary Energy consumption and energy costs. The main advantage is that m-CHP systems are able to recover and use the heat that in centralized systems is often lost. Wide exploitation of these systems is still hindered by high costs and low reliability due to the complexity of the system.

ReforCELL aims at developing a high efficiency (electric efficiency above 42 % and overall efficiency above 90 %) PEM based micro-CHP system through: i) design, construction and testing of an advanced catalytic membrane reactor for pure hydrogen production from hydrocarbon reforming, and ii) design and optimization of all the components for the



integration of the membrane reformer to the fuel cell stack. It is conducted by 11 partners and coordinated by TECNALIA (<http://www.reforcell.eu>).

The main idea of ReforCELL is to develop a novel more efficient and cheaper membrane reactor in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit. In order to achieve this objective, novel stable catalysts and high permeable and more stable membranes need to be developed. Afterwards, suitable reactor design will be realized and tested at laboratory scale for later scaling up to prototype scale (5 Nm³/h of pure hydrogen) and tested in a CHP system.

The connection of the novel fuel processor within the CHP will be optimized by designing heat exchangers and auxiliaries required in order to decrease the energy losses. In addition, a complete lifecycle analysis of the system will be carried out and cost analysis and business plan for reformer manufacturing and CHP system will be supplied.

Introduction to DEMCAMER: Design and manufacturing of catalytic membrane reactors by developing new nano-architected catalytic and selective membrane materials (José Luis Viviente)

The DEMCAMER project aims to develop innovative multifunctional Catalytic Membrane Reactors (MR) based on new nano-architected catalysts and selective membranes materials to improve their performance, durability, cost effectiveness and sustainability (lower environmental impact and use of new raw materials) over four selected chemical processes for pure hydrogen, liquid hydrocarbons and ethylene production:

- Autothermal Reforming (ATR)
- Fischer-Tropsch Synthesis (FTS)
- Water Gas Shift (WGS)
- Oxidative Coupling of Methane (OCM)

Moreover DEMCAMER will bring the proof of concept of these novel catalytic MRs by the set-up and validation of pilot prototypes relevant for each process. It is conducted by 17 partners and coordinated by TECNALIA (<http://www.demcamer.org>).

Scientific and Technical Objectives

- To develop new **membrane materials** with improved separation properties, long durability, and with reduced cost.
- To develop new **nano-architected catalysts** with better performance and at reduced cost.
- 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.



- To validate the new membrane reactor configurations, at semi-industrial prototype level, in the four selected chemical process: ATR, FTS, WGS and OCM.
- 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.

Introduction to CARENA: Pd-membrane based reactors for C1 to C4 conversion (Arend de Groot)

In the past decade the world has experienced a widening gap between the predicted demand for oil and known reserves. The gap has been fuelled particularly by the growth of economies like China and India. Europe relies for more than 70% on imported oil and as a result high oil price are a serious threat to the competitiveness of the chemical industry in Europe. Therefore the chemical industry is looking to turn to novel feeds such as natural gas, coal and biomass to stay competitive. Technologies that are able to use light alkanes (C1 – C4) and CO₂ as feedstocks are necessary. However, light alkanes and CO₂, in contrast to long-chain hydrocarbons from oil, are stable molecules. This makes it difficult to activate and transform them directly and selectively to added value products. Radical scientific and technological improvements are thus required to enable efficient and competitive routes for their use.

In the CARENA Project several routes towards valuable components are investigated. For methane effective conversion of natural gas to syngas and/or hydrogen is the key enabling technology for further conversion to long-chained molecules or olefins. CARENA targets the use of membrane reactors to develop innovative schemes for syngas production for methanol as well as direct conversion of methane to methanol. A novel process concept developed within CARENA aims at (oxidative) dehydrogenation of propane and subsequent selective oxidation of propylene in a propane/propylene mixture to acrylic acid. Reuse of carbon dioxide to replace (new) fossil carbon is a hot topic, but reactions of CO₂ to platform chemicals such as DMC or DME, are strongly limited by equilibrium. This makes the use of membrane reactors to increase the yield of these reactions of special interest.

Within the CARENA project many technological aspects are addressed, including the development of catalyst suitable for the operating conditions in a membrane reactor, development of novel membranes and their improvement for the reactor application and innovative reactor designs. In the presentation the objectives and the results of the CARENA project have been reviewed.



Session 1: Fundamental Aspects of Membrane Technology

Hilde Johnsen Venvik (Norwegian University of Science and Technology), Investigation of fundamental phenomena affecting the performance of thin Pd-Ag membranes

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Alessio Caravella (UniCal, ITM-CNR), Concentration polarization and inhibition by CO in supported Pd-based membranes

The lecture deals with the hydrogen permeation through Pd-based in the presence of both concentration polarization and inhibition by CO. To perform this investigation, we used a model already available in the literature to evaluate the combined effect of these two phenomena on the overall permeation process. Such a model divides hydrogen permeation into several elementary steps, each of which characterized by its own kinetic and transport phenomena. Among these steps, the attention is paid to the competitive adsorption of H₂ and CO on palladium, as well as to external mass transfer (concentration polarisation) and internal diffusion through the selective metal lattice. It is shown an approach based on which the internal diffusion is characterized by an ideal contribution and a non-ideal one, which can be estimated by using an appropriate polynomial form for flux. The overall effect of all this coupled phenomena, including also the presence of a multilayer porous support, influences the permeation rate, expressed in terms of permeance. In the lecture, the effect of polarization and inhibition by CO on the hydrogen permeance is shown in terms of both permeance behaviour with the hydrogen concentration in the feed and concentration polarization coefficient calculated by taking into account the presence of inhibition, which reduce the polarization with respect to the case of external mass transfer only.

José-María Sánchez-Hervás (CIEMAT), Impact of syngas components - CO₂, H₂O, and CO - on hydrogen permeance behaviour over relevant testing times

Palladium membrane reactors have been identified as a promising technology for hydrogen production/purification. They are suitable, for instance, for H₂/CO₂ separation in thermochemical conversion processes and also for use in equilibrium limited reactions in the chemical industry. Palladium is known to be a metal with superior perm-selectivity to hydrogen. Unfortunately the presence of other gas components has a detrimental effect on hydrogen permeation due to a number of inhibition processes such as concentration polarisation, depletion, adsorption, deactivation or hydrogen consumption due to undesired reactions.

This work elaborates on the impact on hydrogen purification and separation of the main components expected to be found in syngas. Experiments were conducted at bench-scale level, using a pre-commercial membrane module supplied by CRI Criterion Inc., over relevant testing times. The effect of different operating conditions and gas environments on hydrogen permeation and recovery is presented including pure hydrogen, binary and ternary mixtures. The effect of pressure and temperature is discussed, as well as the effect of co-existing gases, namely carbon dioxide, steam, carbon monoxide and nitrogen. Finally results about the performance under full synthetic syngas are given.

Further information can be found in the following publications:

- "Hydrogen separation studies in a membrane reactor system: Influence of feed gas flow rate, temperature and concentration of the feed gases on hydrogen permeation" M.M. Barreiro, M. Maroño, J.M. Sánchez Applied Thermal Engineering, 74, (2015), 186-193.
- "Bench-scale study of separation of hydrogen from gasification gases using a palladium-based membrane reactor", J.M. Sánchez, M.M. Barreiro, M. Maroño, Fuel 116, (2014), 894–903.
- "Hydrogen permeation through a Pd-based membrane and RWGS conversion in H₂/CO₂, H₂/N₂/CO₂ and H₂/H₂O/CO₂ mixtures", M.M. Barreiro, M. Maroño, J.M. Sánchez, International Journal of Hydrogen Energy, 39, (2014), 9, 4710-4716.
- "Hydrogen enrichment and separation from synthesis gas by the use of a membrane reactor" J.M. Sánchez, M.M. Barreiro, M. Maroño, Biomass and Bioenergy 35, (2011), S132-S144

Thijs Peters (SINTEF), The performance of Pd-Ag alloy membrane films under exposure of trace amount of H₂S

Highly efficient and cost-effective ultrapure H₂ production can be achieved by integrating H₂-selective membranes in methane reforming (MR) or in water gas shift (WGS) reactors. Various membrane types are being researched for this high temperature H₂ separation, including silica, zeolite, carbon and amorphous alloy membranes. Pd and many Pd-alloys have high solubility (S) and diffusivity (D) of hydrogen, and show great promise as membranes for medium to high temperature hydrogen separation (> ~300 °C). This type of membrane provides the best selectivity-flux combination of all the membrane classes.

The majority of the work related to Pd-based membranes is on the highly permeable Pd-Ag alloy. The drawback is, however, that this alloy may be prone to trace contaminants a cleaned syngas still may contain, such as sulfur species, CO, NH₃, chlorides, cyanides, and heavy metals. For example, even a few ppm of sulphur in the gas reduces the flux drastically due to strong surface adsorption leading to reduced permeability, or even to complete deterioration of the membrane caused by formation of bulk Pd₄S. It is therefore important to assess the stability of Pd-alloy membranes under long-term exposure to trace levels of different contaminants, and to determine their upper acceptable concentration. In addition, it is very important to investigate the short-term tolerance, related flux inhibition and the subsequent H₂ flux recovery during exposure to higher up-set contamination levels. Results of both studies were presented at the conference.

Andreas Goldbach (DICP), Stability of Pd-membranes under practical operation conditions

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Frans van Berkel (ECN), Long term testing of Pd-membranes under methane steam reforming conditions

During the last decade ECN has demonstrated the potential of implementing hydrogen separating palladium membranes in the methane steam reforming (SR) process for hydrogen

generation. In this concept the palladium membrane takes care of the removal of hydrogen, shifting the SR equilibrium towards hydrogen at relatively low operating temperatures (< 600 °C). Lower operating temperatures for methane steam reforming are potentially leading to cost efficiencies and higher energy efficiencies. A major concern in the development of these membrane reactors is the lack of knowledge on the membrane life time under methane SR conditions. Therefore, two ECN Pd-based membranes (0.35-0.44 m² effective length, Al₂O₃-based porous support with either 2 or 4-5 μm thick Pd-layers prepared by electroless plating) equipped with ECN compression seals were tested for 1500-2400 hours under typical SR feed gas associated with a S/C of 3, feed pressure of 27 bar and an operating temperature of 450 °C. The membrane with the 4-5 micron thick Pd-layer showed the best long term performance with a gradual small decrease in hydrogen purity at the permeate side over a test period of 100 days but still remaining at purity levels well above 99%. The observed decrease of the hydrogen purity could be attributed to an increase in leak rate over the membrane. This leak rate was found to be in the Knudsen regime, indicating the gradual formation of nano-sized defects. The distribution of these defects was found to be homogeneously distributed over the length of the membrane. The cause of the defect formation could be found in the grain growth behavior of the Pd-layer. SEM analysis of the surface of the post-test membrane showed that the grain size of the Pd-layer is in the same order as the thickness of the layer. Apparently grain growth has taken place during the long term test where the final grain size is determined by the thickness of the Pd-layer. A consequence of these observations might be that when the grain size reaches the dimension of the Pd-layer thickness the circumventing grain boundary might form a direct connected pathway for leakage from one side to the other side of the Pd-layer. Consequently the grain boundary itself could be the source of the increase in observed nano-scale defects. It is clear that further R&D is required in order to prove this hypothesis and to find ways to diminish this defect formation behavior.

Doug Way (CSM) (Presented by Amanda Lewis (Pall)), High temperature stability of Pd alloy composite membranes and their application to membrane reactors

The integration of Pd-based membranes within catalytic reforming reactors to produce hydrogen has received much more attention during the last few decades. The selective removal of hydrogen from the reaction environment using high temperature membranes allows a membrane reactor to overcome the thermodynamic equilibrium limitation for the reversible hydrogen production reactions. Despite the attractions associated with the use of Pd-based membranes in SMR catalytic reactors, there are still some issues that prevent this technology from being fully commercialized, such as the long term thermal stability and the chemical tolerance of these membranes in real-world mixed gas and reactor environments. In particular, it has been reported in the literature that pure Pd composite membranes can be susceptible to loss of selectivity due to the formation of pinholes when operated at temperatures of 500°C and above. In previous work, we have shown that Pd alloy membranes, such as PdRu, are more thermally stable than pure Pd membranes without heat treatment on identical substrates.

In this work, a ~5.0 μm thick Pd-Ru membrane (area ~ 13.3 cm²), supported on a porous yttria-stabilized-zirconia/stainless steel substrate (ZrOD AccuSep®, Pall Corp.) was used to carry out steam methane reforming (SMR) over a commercial Ni-based reforming catalyst at a temperature of ~580°C and pressures up to 2.9 MPa. Methane conversions in the



membrane reactor ranged from 65 to over 80 %, depending on the reactor's space velocity. The conversions obtained were significantly higher than the thermodynamic equilibrium (~16 % at 580 °C, 2.9 MPa, steam/carbon=3) predicted for the feed composition and process variables. The effect of parameters such as space velocity and reactor pressure on methane conversion and hydrogen recovery were investigated.

The long term operation on this membrane revealed the potential suitability of this Pd-alloy to be a candidate for use in SMR membrane reactors at temperature as high as 580°C. The permeate hydrogen flux was very stable at 580°C, feed pressure of 2.9 MPa, and a steam-to-carbon ratio (SCR) of 3 for more than 1,000 hours of continuous testing. The hydrogen permeate purity remained > 93% over the course of testing. Stable methane conversions as high as ~80% were obtained for the duration of the long term test which may be further improved by optimizing the fluid mechanics of the reactor design or geometry. 1-Dimensional process simulations were carried out and the results suggested that the methane conversion and hydrogen flux during the membrane reactor experiments were reduced by gas phase mass transfer due to concentration polarization effects. Ongoing work will focus on how membrane microstructure affects thermal stability and further optimization and testing of scaled-up Pd-Ru membranes in SMR reactor environments.

Session 2: Manufacturing and Scale-up Challenges

Annarita Salladini (PI), Optimization of porous metal support for Pd-deposition

The application of membrane technology for hydrogen separation is increasingly studied as also documented by a growing research activity. However to move against a real industrial application, a higher reliable level in terms of long time stability as well as standardized manufacturing methods as cheap as simple as possible are required. In this scenario composite membranes on metallic supports due to a better performance in terms of mechanical strength, adhesion, resistance, easy of sealing and assembly seem to be a suitable candidate. One of the main issues in metallic membrane fabrication is represented by the poor quality of porous metal supports which strictly influences manufacturing process and consequently final membrane performance.

The existing commercial support in fact fits well the requirements of other applications such as solid gas filtration and gas distribution but are quite far from membrane manufacturing requirements especially in terms of surface finishing. To overcome this drawback which doesn't allow to apply a thin and dense membrane thickness, different kind of pretreatment need to be applied on commercial supports.

The aim of the lecture is to report a brief state of art in the field of metallic membranes manufacturing, especially for what concern main procedure adopted to modify and upgrade commercial porous support. The lecture is carried out in the framework of the CoMETHy project, whose main focus is the development and construction of a compact multi fuel membrane reformer. Attention is given also to main efforts performed within the project in terms of metallic supports characterization and optimization as well as in terms of new support manufacturing process development suitable for membrane application.

Alfredo Pacheco Tanaka (Tecnalia), Development of Pd-based supported membranes

In order to increase the hydrogen flux and reduce cost, supported Pd based membranes are being developed. The choice of the support is of critical importance in the preparation of thin and defect-free membranes. Surface roughness and presence of large pores inhibit the deposition of thin Pd membranes. It is also important to consider the thermal compatibility of Pd and the supports; at more than 600 °C alumina supports can be reduced to alumina forming an alloy with Pd reducing considerably the hydrogen permeation; however, YSZ support are stable at 650 °C.

Thin supported Pd-Ag membranes have been prepared using physical vapour deposition (PVD) and electroless plating (EP) techniques. Direct deposition of Pd₇₇Ag₂₃ alloy on porous (110 nm) ceramic supports produce membranes with low selectivity, however, Pd-Ag membranes with high permeation and selectivity were prepared by simultaneous EP deposition. Pd-Ag membranes were prepared by ELP to be used in water gas shift reaction (WGS) and auto-thermal reforming of methane (ATM) for the projects DEMCAMER and REFORCELL respectively. The surface of thin Pd membranes are prone to becoming contaminated and mechanically damaged; the mechanical stability can be improved by filling nano-sized pores of a supported ceramic with Pd particles (pore filled membranes) in addition, the amount of Pd used is a fraction of a comparable conventional Pd membrane. In conclusion, in order to prepare defect free thin supported Pd base membranes, it is



important to consider the properties of the support and the method of deposition of the Pd film.

L. Baldassari (Ecorecycling), Pd-recycling and LCA

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Giuseppe Barbieri (ITM CNR, UniCal), Membrane reactors innovating H₂ steam upgrading

An important contribution to the industrial sustainable development can be given by the “green process engineering”. Based on the principles of the Process intensification strategy it can lead to the development and the re-design of new processes more compact and efficient allowing the better exploitation of raw materials, a lower energy consumption, a reduced plant volume, etc.. The membrane technology well pursue these principles and, in this logic, the membrane reactor (MR) technology is going to find more and more application in the energy production plants for the better valuable exploitation of materials such as coal, natural gas, light hydrocarbons as well as biomasses considering these not only as simple energy sources but also as hydrogen sources. In each of these hydrogen production cycles the syngas stream coming out from reformers, gasification plants, etc. contains a large percentage of H₂ (ca. 50%) and CO (ca 45%) and it is traditionally upgraded by water gas shift reaction (WGS) carried out in a two steps process operating in a temperature range of (200-400°C). The first reactor, packed with Fe/Cr catalysts, is followed by a low-temperature one characterized by much higher (ca. 10 times) volume owing to the slower kinetics of Cu/Zn based catalysts operating at low temperature. Pd-based membrane reactors, selectively removing hydrogen, shift the equilibrium conversion of this new reactor type to values higher than those imposed by thermodynamics to traditional reactors.

In this work the advantages offered by a Pd-Ag MR operated in the typical high temperature range for (330-450°C), are theoretically [ⁱ] and experimentally [ⁱⁱ] investigated as function of the main variables whose values are close to those used in the industrial applications. The MR performance, compared with that of a traditional reactor (TR) operated in the same conditions, is evaluated also in terms of new metrics which evidence the advantages offered by MR technology. A CO conversion significantly higher than the thermodynamics upper limit of a TR is achieved, also at high values of GHSV and less than 30% of the reaction volume of a TR is required for achieving a set conversion. The proposed analysis demonstrated how only one stage based on a Pd-alloy MR can replace the two reactors of the Traditional process, arising an intensified process with a smaller reaction volume, higher conversion and GHSV, pure hydrogen recovered.

Moshe Sheintuch (Technion), Reactor modelling, simulation and operating parameters optimization

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Fausto Gallucci (TU/E), Fluidized bed membrane reactors for hydrogen production and CO₂ capture

A novel reactor concept, which combines many advantages of Chemical Looping (CO₂ capture and heat integration) and membrane reactors (pure H₂ separation and process intensification), is proposed in this work. The concept is first evaluated and compared to other novel concepts through a thermodynamic analysis, showing that the Membrane-Assisted Chemical Looping Concept circumvents the drawbacks of the other processes with high reforming efficiencies for H₂ production. In order to obtain a more detailed evaluation of the novel reactor concept, a detailed comparison with the benchmark technology for H₂ production with and without action for CO₂ capture is carried out. The comparison represents a real industrial case including heat exchangers for good heat integration, compressors in order to deliver H₂ and CO₂ at the desired pressure for further applications or steam and gas turbines in order to maximize the performance of the process. Based on realistic assumptions for the three technologies studied, it is determined that a global reforming efficiency in the benchmark technology is about 80%. However, when CO₂ capture is included in this technology through MDEA adsorption the reforming efficiency decreases to 67%. This is explained by the consumptions related to CO₂ capture and the fact that less steam is produced that can be used in further applications. In the novel reactor concept proposed, the reforming efficiency is around 78%, which implies that the cost associated to avoiding CO₂ emissions is strongly decreased and the penalty associated is not as important as in the benchmark technology. In this case H₂ compression represents the main consumption and the process has some technological challenges that should be accounted. Even though slightly lower efficiencies compared to benchmark technology, the novel concept is free-CO₂ emissions and would contribute in controlling the CO₂ concentration in the atmosphere.



Friday 21st November 2014

Session 3: Towards Industrial Applications

Annarita Salladini (PI), Solar assisted reforming and CCS in novel process schemes for H₂ production-techno economic assessment

Under the scenario of hydrogen production coupled with carbon dioxide capture, membrane based architecture may be a suitable and attractive solution providing a retentate stream at high pressure and high CO₂ content. As well known in a traditional steam reforming scheme, carbon dioxide is delivered through a flue gas stream, under low partial pressure thus requiring high capital and energy intensive process for its capture. To reduce emissions, membrane technology may be coupled with a solar energy source thus allowing for a more sustainable process by reducing or avoiding fuel consumption associated to steam reforming furnace.

The lecture is carried out in the framework of CoMETHy project, whose main focus is the development and construction of a compact multi fuel membrane reformer sustained by concentrating solar power plant fed with molten salts. The aim of the lecture is to carry out a techno-economical assessment of different process scheme for hydrogen production and carbon dioxide capture based on membrane technology and solar energy exploitation. The proposed solutions are analysed and compared with a traditional scheme in terms of hydrogen production cost and carbon dioxide capture cost.

Results show that the proposed concept may be effective from a technical as well as from an economical point of view under the hypothesis to solve one of the main drawbacks of solar energy exploitation related to its intermittence. On the other side membrane technology seems to fit well the requirements for carbon dioxide capture allowing for a competitive capture cost.

Markus Haydn (Plansee SE), Metal-supported Pd-membrane for hydrogen production

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Andy Tsai (T3 Scientific LLC), The road to robust Pd-membrane

In this presentation, T3 Scientific presented solutions to two major technical barriers of Pd membrane: long term stability and trace amount of corrosive gases. T3's approach to protecting the Pd membrane from corrosive gases is to provide a protective coating – the MembraGuard™ coating. MembraGuard coating was shown to protect the underlying membrane from high levels (200 ppm) of H₂S. The coating does not show resistance to H₂ flow. It is not affected by the presence of moisture. TEM images showed no cracking or delamination of coating after the coating has been tested extensively with thermal cycling and repeated start and stop. Long term testing data showed that the intermetallic layer – FuseGuard™ worked effectively to prevent intermetallic diffusion. T3 also formulated a higher temperature (> 550°C) version of MembraGuard and FuseGuard. Preliminary results showed that with the high temperature formulation, H₂ flux was stable at 700°C. In conclusion, MembraGuard is chemically and mechanically robust. It protected the



membrane from H₂S. FuseGuard extended both the time scale and temperature range of Pd membrane. Both of these technologies provide robustness to Pd membrane.

Scott Hopkins/Amanda Lewis (Pall corporation), Pd-membrane development at Pall

Pall has a list of issues to address in order to make palladium membranes viable for commercialization. This list includes membranes that are both durable and stable, “easy” scale-up in terms of both membrane fabrication and substrate support, and a thoughtful module design that addresses sealing issues and concentration polarization (amongst other things). Durability and stability are application dependent, but the areas that we’ve identified as most crucial are chemical and thermal resistance, consistent performance, and ability to withstand anticipated temperature and pressure cycling. We are developing novel ternary Pd-based alloys for increased chemical stability in the presences of carbon monoxide and hydrogen sulfide. We are using a high throughput combinatorial screening method that is commonly used to develop catalysts to guide our alloy selection. We have also identified an alloy that has consistent hydrogen flux and purity during constant temperature and pressure cycling.

We are also investigating the ease of boosting production from lab size to pilot to large-scale manufacturing. We are weighing the pros and cons of membrane fabrication techniques: for example, electroless deposition uses inexpensive equipment, but creates a large liquid waste stream that would need to be properly disposed. Pall has performed extensive work on the substrate supports as well as module design. We are able to reproducibly make substrates with a diffusion barrier. Our module design is based on fluid dynamics modeling and addresses concentration polarization. Pall is willing to collaborate and license technology. Please contact us for more information.

Xavier Quek (Johnson Matthey), Pd-membrane activities at Johnson Matthey

Johnson Matthey has been working on Pd membranes since the 1960s. Early work involved both flat sheets and self-supporting tubular Pd membranes for H₂ generators and purifiers for generating high-purity hydrogen for electronic applications. In the 1990s and 2000s, research programmes on thin-film, supported membranes focused on ceramic-supported Pd-alloy membranes, which were studied in various applications such as fuel cells, on-board reformer and coal gasification. In 2013, Johnson Matthey joined a project funded by the US Department of Energy (Grant: DE-FE0004895) entitled, “Engineering Design of Advanced H₂ – CO₂ Pd and Pd/Alloy Composite Membrane Separations and Process Intensification”. The project partners are Worcester Polytechnic Institute (WPI), Johnson Matthey, Membrane Technology and Research Inc. and T3 Scientific Inc.. One of the key objectives of the project is to build, and install at the US National Carbon Capture Centre, a membrane separation module with the capacity to produce 15 to 20 lb of H₂/day. Johnson Matthey’s role is to transfer the WPI Pd membrane laboratory synthesis procedure to an industrial pilot-scale synthesis procedure. This work will aid in the transition to large-scale fabrication of Pd membranes for future applications.

Tony Boyd (MRT), Summary of fluidized bed reactor and membrane experience at Membrane Reactor Technologies

This presentation summarized Pd membrane and reactor work at NORAM Engineering (NORAM) and Membrane Reactor Technologies (MRT). MRT was started in 1998, with NORAM as an equity and engineering partner, based on academic work and patents from the University of British Columbia and the University of Calgary. NORAM purchased MRT in 2012. Various configurations of MRT's autothermal fluidized bed membrane reactor (FBMR) configurations were presented, including a two-bed design that uses circulating solids (SMR catalyst and limestone) to capture CO₂.

The two Pd membranes that MRT / NORAM produce are:

- 15 to 25 μm Planar PdAg foil membranes
- 3 to 10 μm electroless plated PdRu membranes

Recent data from testing of our PdRu membranes indicates enhanced robustness resistance to hydrogen embrittlement over pure Pd. Testing of PdRu membranes has been conducted, with the longest single membrane undergoing over 5000 hours of service. NORAM is now looking to scale up the PdRu membrane sizes and increase the service conditions (currently ~475°C, 10 bar).

Adele Brunetti (ITM-CNR, UniCal), How membrane reactors can affect H₂ production cycles

At early stages of the hydrogen economy that is today becoming more and more a real option for alternative energy production, the demand for hydrogen is foreseen for small-scale and geographically-decentralised volumes. Small production units can be modular, scalable and can provide hydrogen where needed, answering to the market requirements. Distributed production at refuelling stations, using the already present natural gas infrastructure, is therefore viewed as an attractive near to medium-term option.

In this work, the design a new process where a novel WGS Pd-based membrane reactor is integrated in a small scale natural gas reforming system for H₂ production is proposed. Two MR configurations were investigated and their performance were analysed taking into account the concentration polarization phenomena usually affecting the hydrogen permeation. Both permeate and retentate down-streams treatment were designed and various options for their final use were considered. In addition, the environmental impact of this novel technology over the entire life cycle of the processes was evaluated by means of a preliminary life-cycle-assessment, focusing on three impact categories, i.e. Green House Gases (GHG) emissions, Resources depletion, Water withdrawal.

Overall, the integrated system resulted in more intensified one than the reference technology, achieving higher CO conversion with less feedstock. Although, the concentration polarization effect reduced of only 10.5% the hydrogen permeation, this technology allows the targets of CO conversion and hydrogen recovery to be reached. Finally, WGS-MR technology resulted in a 8-12% reduction of GHG emissions and a 5% reduction of the impact on resources depletion, whereas a 39% increase of water withdrawal was registered with respect to reference technology.



Leonardo Roses (HyGear), Simulation, integration and assembly of pilot-scale fluidized bed membrane reactors

This presentation gives an overview of the activities carried out at HyGear in the framework of two project partially funded by the EU: Projects ReforCELL (FP7/FCH-JU) and DEMCAMER (FP7). Both projects make use of palladium based membrane reactors for hydrogen production. For each project we discuss the system layout, the reactor specifications, characteristics about the simulation model, the reactor design and integration into the system.

ReforCELL project employs a fluidized bed autothermal reforming membrane reactor. The reactor is designed for 5 Nm³/h of hydrogen output from reforming of natural gas at 7 bar and 600 °C. At nominal output the hydrogen recovery factor is around 90 % and increasing at partial loads. DEMCAMER project employs a water gas shift membrane reactor for production of hydrogen from a reformat stream. The reactor is designed for 5 Nm³/h of hydrogen, operating between 320 and 500 °C and using less than 0.2 m² of Pd/Ag membrane. Hydrogen recovery is above 90 % and CO conversion above 95 %. Nominal testing pressure of the system is 6 bar but the reactor alone is designed for up to 8.5 bar.

The economic outlook of the use of Palladium membranes for hydrogen purification is strongly dependent on the target market: Mainstream bulk hydrogen production or alternative markets? In mainstream sector the benchmark technology (PSA) has well established costs. Membrane solution should still put focus on cost reduction and increasing durability.

Giampaolo Manzolini (Polytecnico de Milano), Techno-economic optimization of Pd-based membrane reactors in PEM micro-CHP systems

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Spyros Voutetakis (CERTH), Integrated membrane reactor testing and modeling

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Session 4: Alternative Applications

Roland Dittmeyer (KIT), Overview on Pd-membrane reactors (for dehydrogenation)

The generic concepts motivating the use of Pd membranes in chemical reactors are explained, and the current R&D activity in the field of dehydrogenation using membrane reactors is assessed. The previous experimental and theoretical work carried out by the authors on the use of Pd membranes for industrial dehydrogenation processes is reviewed. Results obtained on ethylbenzene dehydrogenation and propane dehydrogenation are presented and evaluated with a view to their practical significance. A new concept for using a liquid organic reaction cycle for heat storage involving methylcyclohexane dehydrogenation to toluene in a Pd membrane reactor is introduced. The main advantages of microchannel systems for realizing compact membrane reactor modules are explained, and recent results obtained on this application in a small microstructured concept module are presented and discussed. With a view to the scale-up of such systems, the design of a microchannel membrane reformer developed by the authors is shown.

In conclusion, kinetic inhibition by product adsorption or low driving force due to high dilution with steam may greatly reduce the performance of dehydrogenation membrane reactors when higher conversions are targeted. Both may lead to prohibitively large reactor volumes. In the absence of steam, carbon formation on the catalyst and on the Pd membrane surface as well as inhibition of the hydrogen permeance induced by the unsaturated products bring about major challenges with regard to long-term operation and regeneration of catalyst and membrane. This is most obvious for propane dehydrogenation. Methylcyclohexane dehydrogenation looks more promising. Microchannel membranes reactors could lead to very compact and efficient systems provided stable catalyst performance and in place regeneration of catalyst and membrane can be established.

Thijs Peters (SINTEF), Investigation of Pd-based membranes in propane dehydrogenation (PDH) processes

Pd-based membranes have potential applicability in the PDH process to selectively remove hydrogen. In the framework of the EU-7FP project CARENA, SINTEF has evaluated H_2 flux values and coke formation kinetics applying representative gaseous feed mixtures under varying operating conditions. From these experiments, it is clear that coke formation is very likely under the operating conditions required for an integrated catalyst and membrane system, *i.e.* temperatures of 450-500 °C. For a viable application of Pd-based membranes to the PDH process, a practical membrane regeneration procedure should be developed, preferably with an integrated process of catalyst regeneration.

However, coking could be limited at lower temperatures, and a decrease to at least 300 °C, or preferably, to 250 °C is required to obtain a sufficiently stable membrane operation in the conditions observed in a non-integrated process design. This process design is investigated experimentally. In these tests, the effect of steam content on catalyst and membrane activity and stability were investigated. Results show that steam is required to obtain good catalyst stability, but that the produced H_2 independent on steam content between 7 and 20%. A stable membrane performance is obtained at 200 °C at HRF-values varying from 38-50%.

Emma Palo (KT), Novel process scheme for selective propane dehydrogenation

Olefin compounds (alkenes) are widely used in a number of chemical industries. Among them propylene is the world's second largest petrochemical commodity, being the precursor of polypropylene, which is used in such everyday products as packaging materials and outdoor clothing. Currently, most propylene is produced by steam crackers (55%) as by-product of ethylene. Refinery Fluid Catalytic Cracking units also contribute to a significant portion of global propylene supply (30%). Other on-purpose propylene supplies contribute 15% of global propylene supplies in the form of propane dehydrogenation (PDH), methanol-to-olefins (MTO), and metathesis. The big increase in the global demand for propylene expected in the oncoming years is pushing to the intensification of production routes aiming to the product of propylene as primary product. Selective PDH is believed to have a great potential as a propene booster in the future.

In propane dehydrogenation, the thermodynamic constraints of the reaction limit alkane conversion, hence the necessity to operate at high temperature in order to reach a sustainable reactant conversion. In spite of the huge efforts into the direction to increase process selectivity, avoiding in particular coke formation, the severe operating conditions still lead to coke deposition on the catalyst, thus to its deactivation. This is the reason why in the commercialized process a periodic regeneration of the catalyst is required. The possibility to strongly decrease the amount of carbonaceous compound deposited on the catalyst is linked to the possibility to attain sustainable propane conversion at lower temperature, lower than 550°C, overcoming the thermodynamic limitations. One way is represented by the use of membrane reactors, in which the chemical reaction is coupled with the separation of one of the end products, such as hydrogen. In this manner, it is possible to shift the reaction to the right side and consequently the conversion rate or final product yield may be enhanced.

This lecture was performed in the framework of the CARENA project, where the selective propane dehydrogenation is considered as the upstream step for acrylic acid production. The aim of the lecture is to report all the main aspects that should be considered when developing a process scheme for propane dehydrogenation assisted by membrane for hydrogen separation. Attention is given to catalyst and membrane performance in terms of activity and stability and to type of integration of membrane with reaction environment.

Emma Palo (KT), Novel process scheme for syngas production for gas to liquid processes

The contribution is due in the framework of the European project "NEXT-GTL", the main aim of which was to address the main cost drivers and technical barriers of the conventional GTL process, in particular reducing the cost and energy consumption of syngas production step. A novel process scheme based on catalytic partial oxidation (CPO) stages in series for syngas production was developed by KT. The CPO reactors were followed by H² selective membranes operating at low temperature. The overall scheme enables for a very high reaction unit compactness, for lower operating temperature and thus on the whole for less stressing operating conditions for CPO catalyst.

Experimental tests to evaluate the performance of such architecture were performed at the pilot plant in Chieti Scalo, KT owner, where in the former configuration of steam



reforming operating at low temperature and assisted with membrane for hydrogen separation, a CPO reactor was installed.

The CPO reactor was tested with pellets catalyst and honeycomb monolith shaped catalyst, and the tests evidenced the big importance and influence of the catalyst support on the temperature profile established along the catalytic bed. The performance of the overall architecture evidenced a global reduction of 50% in oxygen consumption. These results confirm the potential application of such architecture in processes like Fischer-Tropsch synthesis.

