# CAtalytic REactors based on New mAterials (CARENA)

## 1: Executive summary:

### European CARENA project speeds up implementation of membrane reactors

*The CARENA project is a large EU-funded collaborative project to create technologies enabling efficient conversion of light alkanes and $CO_2$ into higher value chemicals. To reduce the dependency of the European community on imported oil, the CARENA project promotes the implementation of catalytic membrane reactors in the European chemical industry.*

## 2. Summary description of the project context and objectives:

Progress in materials, design of nano-architectures and novel designs of membrane reactors are brought together to enable the development processes. To address both scientific and technological challenges, CARENA brings together a strong European consortium with top level universities, R&D centres, industrial technology providers, chemical producers and innovative SME's. The main benefits to the chemical industry in Europe are to:

- Create new possibilities for the use of cheaper, less reactive raw materials.
- Reduce environmental impact, energy and raw materials consumption by increasing process selectivity, creating innovative process flow schemes and reducing the number of process steps.
- Reduced process risks due to the use of these new and/or more efficiently integrated processes.

The objective of the CARENA project is to develop and implement novel nano-structured materials and optimized membrane-reactor based chemical processes.

**New C1-C4 value chains**

In the past decade the world has experienced a widening gap between the predicted demand for oil and known reserves fuelled particularly by the growth of new economies like China and India. High oil price may particularly affect the competitiveness of the chemical industry in Europe, relying for more than 70% on imported oil. In a global environment with higher cost of naphtha from crude oil and higher cost of $CO_2$, the chemical industry may need to turn to novel feeds such as natural gas, coal and biomass to stay competitive. Technologies that are able to use as feedstocks light alkanes (C1 – C4) and $CO_2$ are needed. However, light alkanes and $CO_2$, in contrast to long-chain hydrocarbons from oil, are stable molecules that are difficult to activate and transform directly and selectively to added value products. Radical scientific and technological improvements are thus required to enable efficient and competitive routes for their use.

**Membrane reactors**

Process Intensification plays a crucial role in overcoming these challenges. Development of catalytic membrane reactors opens new pathways for materials chemistry and processes, as for example recently reported by the European Platform for Sustainable chemical industry (SusChem). According to the European Roadmap Process Intensification published in 2008 and based on the contribution of more than 50 international experts in the field, membrane reactors are one of the leading process intensification technologies. Well known examples are reactors using selective membranes to remove one reactant from the reaction medium and non-selective membrane reactors, which supply reactants in a regulated way or create a well defined reaction interface. The development of membrane bioreactors in the field of water treatment and effluent during the last fifteen years shows that success is often the sequel of stakeholders' decision and of the efforts made to serve the stated objectives.

## The consortium

To achieve competitiveness and sustainability of new chemical processes through the development of highly innovative nano-structured materials and optimized membrane-reactors, scientific excellence needs to be combined with industrial know-how of leading businesses. CARENA brings together companies and institutes from 8 European countries. European chemical companies as **AkzoNobel** and **Arkema** ensure a strong industrial leadership to the project. Technology providers and developers include **Johnson Matthey**, **StGobain**, **KT, Linde, Acktar** and **PDC**. Scientific excellence is strengthened with top-level academic partners and research institutes: **CEA**, **ECN**, **SINTEF, CNRS-IEM**, **CNRS-IRCE, Diamond, Technion, Universities** of **Salerno, Twente** and **Hannover**. The participation of the **EMH** shows the ambition to link the project to the part of the European Research Area (ERA) associated to membrane technologies, following recommendations issued from the NanoMempro network of Excellence. (NMP - FP6).

## Scope of the CARENA Project

The CARENA project focuses on 3 feedstocks:

- Methane
- Propane
- $CO_2$

**Methane** is used in the current chemical industry mainly as a feedstock for production of hydrogen and base chemicals such as methanol and ammonia. A mayor development is the use of natural gas for liquid fuel production through the Fischer-Tropsch process. However, effective conversion processes from natural gas to syngas and/or hydrogen remain the key enabling technology for further replacement of oil by natural gas. CARENA targets both the use of membrane reactors to develop innovative schemes for methanol production as direct conversion of methane to methanol.

In the conventional approach **propane** is converted to acrylic acid in two steps with purified propylene as intermediate. A novel process being developed within the CARENA project aims at (oxidative) dehydrogenation of propane and subsequent selective oxidation of propylene in a propane/propylene mixture to acrylic acid.

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Reuse of **carbon dioxide** receives much attention. CARENA investigates two routes which could greatly enhance reuse of $CO_2$ in the chemical industry: direct conversion of $CO_2$ into dimethyl carbonate (DMC) and methanol (MeOH). As both reactions are strongly limited by equilibrium, the use of membrane reactors is of special interest. Through lab-scale testing of a system integrating both catalyst and membranes, the project focuses on delivering the proof-of-principle for membrane reactors in these applications.

## 3: Description of main S & T results/foregrounds from the CARENA project

The CARENA project was completed in May 2015. The project has achieved results in many fields, including the development of novel membranes and catalyst, membrane reactor design and testing, process design and evaluation and industrial methods to characterize and manufacture membranes. Ultimate goal of the CARENA project is to help bring the concept of membrane reactors to industrial realisation. To evaluate the progress achieved through the CARENA project, the essential reference is the progress required to achieve this goal.

### Challenges in scaling up membrane reactors

The principle of membrane reactors has been demonstrated frequently on lab-scale, for example for esterification reactions, for water-gas shift, for reforming and other reactions where the operating windows for membrane and catalyst overlap. What (more) is required to make membrane reactors and industrial reality?

- **Life-time**: Going from lab-scale to a pilot sets increasingly higher demands on the lifetime of both catalyst and membranes. For most types of membranes achieving a commercial life-time target (> 10 000 hours) is still far from reality, in particular in "real" industrial mixtures.
- **Reproducible and cost-effective fabrication cost.** Many types of membranes, requiring very specific functionalities, require high cost materials. Driving down cost of membranes requires membrane design reducing the amount of material needed (e.g. by use of thin layers and high fluxes). However, also the development of fabrication technology which can be applied on an industrial scale is an essential step in commercializing the technology.
- **Operating windows**: combining membranes and catalyst in a closed architecture[1] requires operating both under the same conditions. For many reactions the operating windows do not overlap and novel material are required apply a closed architecture. Even applying an open architecture, minimizing the gap between the operating window for both steps is necessary to reduce the operating and investment cost for the process.
- **Process and reactor architecture**: the choice between the different degrees of integration of the process architecture depends on many different factors. No clear methodologies exist to select the optimum configuration. Nonetheless, the choice of architecture is essential in terms of performance and cost of the total systems.
- **Scale-up**: the lab-scale process serves to demonstrate the principle of enhanced yield. Translating the results of the single-tube test to a viable reactor concept requires solving many issues which are circumvented while lab-scale testing. Sealing, supplying or removing reaction heat while maintaining the desired temperature profile, uniform distributions of flows over al large number of tubes are examples of issues which need to be addressed in scaling up from a single tube to a reactor design.
- **Process design**: Using a membrane reactor integrating several process steps, tends to simplify the process scheme. In reforming for example a single membrane reactor unit may replace as much as 4 single unit operations. Nonetheless the membrane reactor will generally remain part of a complex process. As the membrane reactor process will be different from the highly conventional plant, the

[1] In a closed architecture the membrane and catalyst are integrated into a single unit, in the open architecture separation and reaction occur sequentially in a series of separation and reaction steps

need to optimize the membrane reactor with respect to investment and operating expenditure requires a thorough understanding of the membrane reactor unit operation and its integration.

The main goal of the CARENA project is to make an important step in scaling-up the membrane reactor technology and bringing it to a higher TRL level. This involves prototype testing to assess the performance of the combination of membrane and reactor, but also addressing the much broader range of challenges indicated above. Below we discuss the progress achieved in the CARENA project per topic:

1. Testing prototypes
2. Developing applications
3. Closing the gap between membrane and catalyst using novel materials
4. Modelling & fundamentals
5. Membrane reactor design
6. Membrane application and membrane scale-up

Part of the information developed in the CARENA project, in particular on testing of prototypes is confidential, but a large part is also public. Where the results are confidential we summarize the activities, for public results we report in more detail and refer to further reading.

## 1) Testing Prototypes

The primary focus of the CARENA project was to validate operation of catalytic membrane reactors for several application through prototypes. The scale on which to validate the prototype varied with the TRL level.
The membrane reactor application which furthest developed, as a classical example of the membrane reactor, is hydrogen production using palladium membranes. In the CARENA project the application of Pd membranes for the production of hydrogen was tested at a multi-tube scale, representing down-scaled version of full-scale design for different types of process architecture. Testing of the *non-integrated* reactor (using separate units for reaction and separation, see below) was carried out at KT's Chieti test-site in a system designed for 20 Nm3/h hydrogen production. The test of a fully integrated reactor at ECN, was carried out with a membrane reactor containing 1 $m^2$ of membrane area and a design capacity of 2-5 Nm3/h of hydrogen. For other reactions catalytic membrane reactors were tested at a lower scale. A full overview of the prototype testing in the CARENA project is shown in the table below.

*Table 1: overview of prototype testing in CARENA*

| Prototype | Scale | Comments |
|---|---|---|
| Non-integrated membrane reactor for hydrogen production | KT's test facility is designed for 20 Nm3/h hydrogen production | Activities included structured catalyst development and construction of membrane module. Experiments based on extensive process evaluations and full-scale design. |
| Integrated membrane reactor for hydrogen production | 1 $m^2$ membrane area, hydrogen production 2-5 $Nm^3/h$ | 1000 hours of testing completed. Reactor design validated. Test results have been partly presented [1]. |
| Propane dehydrogenation | 0.25 kg/h test unit | Several alternative configurations developed. Test of non-integrated system. |
| Oxidative Coupling of Methane | Single-tube catalytic membrane reactor | Unique test-unit equipment built and operated to achieve good control of the hydrodynamics and the temperature. |
| Methanol from $CO_2$ and $H_2$ | Single-tube catalytic membrane reactor | Improvement of conversion shown. Experiments performed over range of temperatures and pressures (up to 40 bar) |
| Direct Methane-to-Methanol conversion | No experimental work on membrane reactor. | Techno-economic analysis lead to a no-go for further development |

In addition to the prototypes above, which test the integrated membrane and catalyst, much additional work was done on the membranes. An important aspect was the selection and testing of membranes under the specific conditions encountered in the membrane reactor. Especially critical are the temperature range in which membranes operate and the composition (e.g. presence of steam, $CO_2$ or contaminants)

- For the reaction of **methanol from hydrogen and $CO_2$**, the membrane prepared for this application and a novel catalyst where able to operate at comparable conditions. This effectively closed the gap between reactor and membrane separation operating windows. At the same time, other types of membranes, which were already able to operate at the required conditions, could be excluded based on the lack of selectivity determined experimentally.
- Experimental results confirmed coking is very likely under **propane dehydrogenation** conditions using Pd membranes. Several strategies to reduce coking were investigated. Both the impact of operating conditions as well as a number of innovative approaches have been investigated.
- A catalytic membrane was prepared for **di-methyl carbonate** (DMC) production by coating the catalyst on a membrane. The specific membrane was a SOD membrane prepared by LUH showing interesting selectivity for this reaction. The functionality of the membrane reactor was however not tested experimentally. These tests were given a lower priority as a result of the less positive outcome of the techno-economic analysis.
- Oxygen conducting membranes were developed and tested extensively on several scales to verify the oxygen flux. The flux is considered as a critical parameter for the development of a reactor for **oxidative coupling of methane**. Test under relevant conditions were carried out both on planar and up-scaled tubular membranes. Developments included (industrially applicable) technologies to coat catalyst layers reproducibly on the membranes.

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| Key Message “Prototypes” | The CARENA project has validated catalytic membrane reactor prototypes on different scales, from small membranes coated with catalyst to pilot plant testing, depending on the initial technology readiness level. The scale of testing and the duration over which tests have been carried out demonstrate the progress made in the underlying fields. |

## 2) Developing applications

The CARENA project considered a number of applications:

- Reforming of natural gas followed by conversion of the syngas to methanol
- A novel route from Propane to Acrylic Acid
- Methanol production from $H_2$ and $CO_2$
- DMC production from methanol and $CO_2$

For all these applications novel process schemes have been developed and techno-economic evaluations carried out.

*Steam methane reforming*

- Process schemes for both the integrated and non-integrated concepts have been finalized and compared to the conventional steam methane reforming scheme for methanol synthesis.
- Very extensive work was done on the comparison of the cost of methanol and on the equivalent and the actual natural gas consumption per ton produced syngas to identify the key cost factors.

*Acrylic Acid from Propane*

A novel integrated process scheme to produce acrylic acid from propane was designed, taking into account the management of impurities in the loop.

- Data collected from lab scale, pilot plants and industrial plants used for the process design and techno-economic evaluation of the propane to acrylic acid with the open-architecture process.
- Steady-state and non-steady-state simulation studies of the PDH reactor have been conducted. The studies clarify how the membrane reactor architecture – integrated, non-integrated or a combination of the two – depends on the optimal operating temperature and rate of deactivation of catalyst and membrane.

*Methanol production from $CO_2$ and $H_2$*

For the Methanol production from $CO_2$ and $H_2$ at the start of the project the operating window of the catalyst and the membrane showed a wide gap. An improved catalyst and membranes operating in a wider temperature range where successfully investigated at SINTEF, UT, Salerno and ECN. These experimental data where used to carry out a techno-economic evaluation of the processes.

Further techno-economic assessments and process designs carried out in the CARENA project included for DMC production, Oxidative coupling of methane and the direct methane-to-methanol (MTM) route.

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| Key Message "Applications" | The value of techno-economic analysis depends strongly on the assumptions which have to be made. Assessments made with in the CARENA project could build on the broad range of expertise from the partners cooperating in the studies (nearly all partners were involved in techno-economic assessments) and relied on a vast body of experimental work including catalyst, membrane and prototype testing. The techno-economic analysis within CARENA represents a unique effort bringing together all these elements. |

Publicly available information on Applications

**CARENA reports:**

- Preliminary heat and material balance *(for the conversion of propane to acrylic acid)* (PDC)
- Economic evaluation of the novel integrated process (*for the conversion of propane to acrylic acid*) (PDC)
- Techno-economic evaluation of alternative processes (*for MeOH and DMC production*) (Akzo)

## 3) Closing the gap using novel catalyst and membranes

In developing CMRs the possible **mismatch in operating windows** between the membrane and the reaction, as illustrated in Figure 1, is of utmost importance. For example because the lifetime of a membrane does not allow operating at a temperature required for a good conversion of the reaction (catalyst activity). Different approaches have been followed in the CARENA project.

- Expanding the overlap in operating window by working on the reaction window, e.g. by creating new reactor designs, developing novel catalysts and/or membranes architectures;
- The overlap can also be enhanced by working on the membrane window, e.g. by improving the performance of the membranes.

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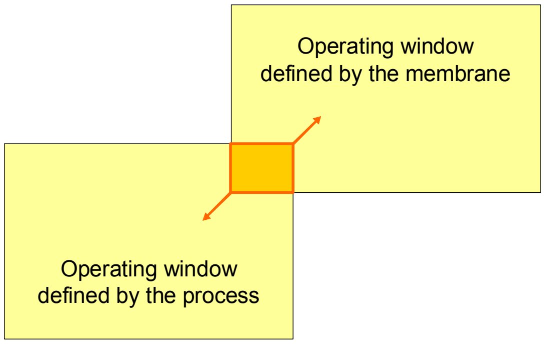
The novel reactor designs and membrane architectures are discussed below. Here we give an overview of the activities on novel membrane and catalyst materials in the CARENA project.

*Figure 1:* Increasing the overlap in operating windows of membrane and reaction is the driving force of CARENA




*Novel membrane materials*
A broad range of novel materials and membranes has been developed in the CARENA project. The approaches followed within the CARENA project include:

- Zeolite membranes;
- MOF membranes;
- iPOSS membranes;
- Dense ceramic hydrogen transport membranes;
- Ceramic supported polymer membranes;
- Other including amorphous SiC,.

Some selected highlights are:

- For the selective separation of water from a reaction mixture at higher temperature (150-200 $^{o}$C) novel approaches have been applied successfully. For example zeolite membranes (LTA) have been fabricated with excellent selectivity by synthesizing the membranes layer-for-layer. Other novel approaches used within the CARENA project include micro-wave assisted synthesis of zeolite membranes and new methods to produce mixed matrix membranes.
- Novel materials applied with success to make selective membranes include metal organic frameworks (MOF's). As an example, membranes based on ZIF-95 were shown to have a good selectivity for hydrogen separation. As the membranes can be operated at higher temperatures, the membranes are potentially suitable for the propane dehydrogenation application, as there coking behaviour is expected to be superior to the state-of-the-art palladium based membranes.
- Hybrid organic-inorganic membranes have been developed based on polyhedral oligomeric silsesquioxane cages (POSS) molecules bridged by imide chains to create a temperature-stable material for which the gas separation properties can be tuned.

However, the work done on novel materials in CARENA is too broad for a short summary and we refer to the large amount of detailed publicly available information on these developments given below.

*Catalyst development*
In general the conditions under which the catalyst operates in a membrane reactor is different from those encountered in the conventional design. Therefore, new catalysts need to be developed or existing catalyst modified to operate at the novel conditions. Successful development of new catalyst in the CARENA project included catalyst for :

- Propane dehydrogenation: achieved objectives include low coking and stable operation at lower temperature.
- DMC synthesis: A catalysts for which is highly active operating temperature of the membrane.

- Hydrogenation of $CO_2$ to methanol - A catalysts for which is sufficiently active and shows less catalyst deactivation.
- Oxidation of propylene to acrylic acid. Key requirement is that the catalyst is selective in under the very different composition in the new process design
- Methane reforming. A catalyst able to operate at low temperature and under hydrogen lean conditions.

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| Key Message "Closing the Gap" | For many membrane reactor applications there is a gap between the operating window of the catalyst and the membrane. Development of novel membrane materials able to extend the currently available operating window, is necessary. Within the CARENA project a number of new approaches have been developed making a step towards closing the gap.<br>Although in all application considered in the CARENA project, standard (commercial) catalyst are available, the work in the project showed that the specific development of the catalysts for the relevant conditions leads to substantial improvements in performance. It clearly shows the need to develop novel catalyst as integral part of the development of membrane reactors. |

Publicly available information on novel membranes and catalyst

**Key Publications**


**Leibniz University of Hannover**: J. Caro, *Are MOF membranes better in gas separation than those made of zeolites?, Current Opinion in Chem. Engin. Sci.,1 (2011) 77-83.*

**Leibniz University of Hannover**: A. Huang, N. Wang, J. Caro, *Seeding-free synthesis of dense zeolite FAU membranes on 3-aminopropyltriethoxysilane functionalized alumina supports*, Journal of Membrane Science, 389 (2012) 272-279.

**Leibniz University of Hannover**: A. Huang, N. Wang, J. Caro, *Synthesis of multi-layer zeolite LTA membranes with enhanced gas separation performance by using 3-aminopropyltriethoxysilane*, Micropor. Mesopor. Mater. 164 (2012) 294.

**Leibniz University of Hannover**: A. Huang, Y. Chen, N. Wang, Z. Hu, J. Jiang, J. Caro, *A highly permeable and selective zeolitic imidazolate framework ZIF-95 membrane for H2/CO separation*, Chem. Commun. 48 (2012) 10981.

**University of Twente:** Raaijmakers, M. J. T., Hempenius, M. A., Schön, P. M., Vancso, G. J., Nijmeijer, A., Wessling, M., & Benes, N. E. (2014a). *Sieving of hot gases by hyper-cross-linked nanoscale-hybrid membranes*. Journal of the American Chemical Society, 2013, 136(1), 330–335. doi:dx.doi.org/10.1021/ja410047u

**University of Twente:** Raaijmakers, M. J. T., Wessling, M., Nijmeijer, A., & Benes, N. E. (2014b). *Hybrid Polyhedral Oligomeric Silsesquioxanes–Imides with Tailored Intercage Spacing for Sieving of Hot Gases*. Chemistry of Materials, 2014, 26(12), 3660–3664. doi:10.1021/cm500691e

**Leibniz University of Hannover**: Y. Liu, N. Wang and J. Caro, *In situ formation of LDH membranes of different microstructures with molecular sieve gas selectivity*. J. Mater. Chem. A, 2014, 2, 5716

**Leibniz University of Hannover**: Y. Liu, N. Wang, L. Diestel, F. Steinbach, J. Caro, *MOF membrane synthesis in the confined space of a vertically aligned LDH network*,Chem. Comm.,50 (2014) 4225-4227

**Leibniz University of Hannover**: Y. Liu, N. Wang, Z. Cao, J. Caro, *Molecular sieving through interlayer galleries*, J. Mater. Chem. A, 2 (2014) 1235-1238

**Leibniz University of Hannover**: N. Wang, Y. Liu, A. Huang, J. Caro, *Supported SOD membrane with steam selectivity by a two-step repeated hydrothermal synthesis*, Micropor. Mesopor. Mater., 192 (2014) 8-13

**Leibniz University of Hannover**: Y. Liu, N. Wang, J.H. Pan, F. Steinbach, J. Caro, *In situ synthesis of MOF membranes on ZnAl-CO3 LDH buffer layer-modified synthesis*, JACS,136 (2014) 14353-14356

**Leibniz University of Hannover**: N. Wang, Y. Liu, A. Huang, J. Caro, *Hydrophilic SOD and LTA membranes for membrane-supported methanol, dimethylether and dimethylcarbonates synthesis*, Micropor. Mesopor. Mater., 207 (2015) 33-38.

**Leibniz University of Hannover**: N. Wang, Y. Liu, Z. Qiao, L. Diestel, J. Zhou, A. Huang, J. Caro, *Polydopamine-based synthesis of a zeolite imidazolate framework ZIF-90 membrane with high $H_2/CO_2$ selectivity*, J. Mater. Chem. A, 3 (2015) 4722-4728.

**University of Twente:** M. J.T. Raaijmakers, M. Wessling, A. Nijmeijer, N. E. Benes, *Spotlight on Recent JACS Publications: Hybrid ultrathin films can handle the heat*, Journal of the American Chemical Society, 2014, 136 (1), pp 3–3

**CNRS-IEM:** Martin Drobek, Mikhael Bechelany, Cyril Vallicari, Adib Abou Chaaya Christophe Charmette, Claudia Salvador-Levehang, Philippe Miele, Anne Julbe, *An innovative approach for the preparation of confined ZIF-8 membranes by conversion of ZnO ALD layers*, J. Mem. Sc., 2015,75, 39-46.

**University of Twente:** Michiel J.T. Raaijmakers, Emiel J. Kappert , Arian Nijmeijer, Nieck E. Benes, *Thermal imidization (kinetics) of hybrid polyPOSS-imide membranes*, Macromolecules, 2015, 48(9),pp3031-3039

**CARENA reports:**

- Report on the development of model structured catalysts to perform kinetic and/or mechanistic studies (IRCE-Lyon)
- First progress report on innovative asymmetric membranes (LUH)
- Second progress report on innovative membranes for evaluation in WPs 1-2-3 (SINTEF)

## 4) Modelling & fundamentals

As part of the multi-scale approach underlying the project (see Figure 2), the modelling activities in CARENA have extended over a wide range of scales. From the modelling the process or plant design to modelling a single atom adsorbs on the surface of a Pd membrane.

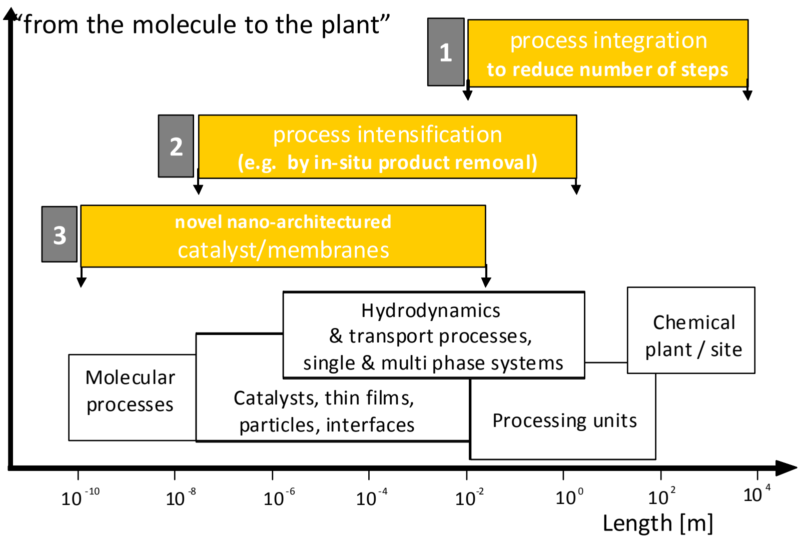


**Figure 2:** Multi-scale approach in CARENA linking materials, reactors and processes

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On the **process design** In particular extensive work was done on methane reforming and on the route from propane to acrylic acid. Modelling methane reforming for methanol production with and without membrane reactors was used to compare a large number of different configurations to understand the merits of the different designs. For propane-to-acrylic acid, a completely new design of the process loop resulted based on the knowledge generated in the project.

On the scale of **unit-operations** modelling work included:

- Steady state CMR models for use in process design for different types of membrane reactors.
- Extensive modelling of a propane dehydrogenation reactor to identify the optimal reactor architecture, specifically in relation to the decrease in catalyst activity over time as result of coking. The modelling allowed to study alternative membrane architectures and operating modes (e.g. sweep).

To determine the optimum configuration of catalyst and membrane in a membrane reactor requires modelling of the reaction and transport phenomena on a micro-scale. An good example of such work in the CARENA project is a generalized analysis made to determine the benefits and disadvantages of placing the catalyst on the membrane or adjacent to the membrane. The analysis, which considers variation of critical parameters such as equilibrium constants and transport properties, shows that in some ranges of these parameters one configuration is optimal, while in others the difference in expected performance between the two configurations is very small.

On the smallest scale, that of the **molecular scale**, modelling worked focused on:

- Unravelling reaction mechanisms fo the reaction to di-methyl carbonate and the oxidative coupling of methane.
- Prediction of transport and inhibition of Pd membranes due to adsorption of reactants and products was carried out using computational modelling with dynamic functional theory (DFT);

On the molecular scale much effort was devoted to modelling combined with measurements of material properties. Having Diamond as partner in the consortium, enabled very innovative experiments where materials could be studied under the relevant reaction conditions. For example combined XAS/MS experiments performed different mixed oxides materials shows the oxidation state of cobalt and iron as a function of the operating conditions. By the combined XRD/XAS approach, the structure of mixed oxide materials was studied by looking at the long-range order of crystalline species and local structure of the whole sample under the same oxidising conditions. Improving understanding of oxygen non-stoichiometry of BSCF perovskite.

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| Key Message “Modelling & Fundamentals” | Although there has already been much work done in the area of modelling and determination of fundamental material properties, the CARENA project shows the important role modelling and experimental characterization can play in scale-up. Scale-up requires understanding many novel aspects of membranes, catalysts and their interaction. It should be noted, as the CARENA project illustrates in a positive way, that the effectivity and relevance of this type of work a is highest if it is driven by the actual questions arising from the development and scale-up of membranes and reactors. Given the broad field of possible modelling and characterization approaches, creating focus on the relevant issues is best achieved in projects allowing for such an integrated approach. |

Publicly available CARENA results on Modelling & Fundamentals

**Key Publications**

**Technion**: E. D. German, H. Abir, and M. Sheintuch, *A Tunnel Model for Activated Hydrogen Dissociation on Metal Surfaces*, J. Phys. Chem. C 2013, 117, 7475−7486

**Technion**: O. Nekhamkina, M. Sheintuch, *Effective approximations for concentration-polarization in Pd-membrane separators*, Chem. Eng. J, 260, 2015, 835-845.

**Technion**: H. Abir, M. Sheintuch, *Modeling $H_2$ transport through a Pd or Pd/Ag membrane, and its inhibition by co-adsorbates, from first principles*, J. Mem. Sci., 466, 2015, 58-69

**CARENA reports:**

- Implementation of a CMR design tool (Technion)
- Catalytic setups to measure intrinsic kinetics for methane oxidation reactions and DMC synthesis (IRCE-Lyon)
- Cells to perform in-situ characterization by impedance spectroscopy and by EXAFS/XANES spectroscopy (IRCE-Lyon)
- Kinetic model for selected catalysts and catalytic membrane to support the design of the membrane reactors (IRCE-Lyon)

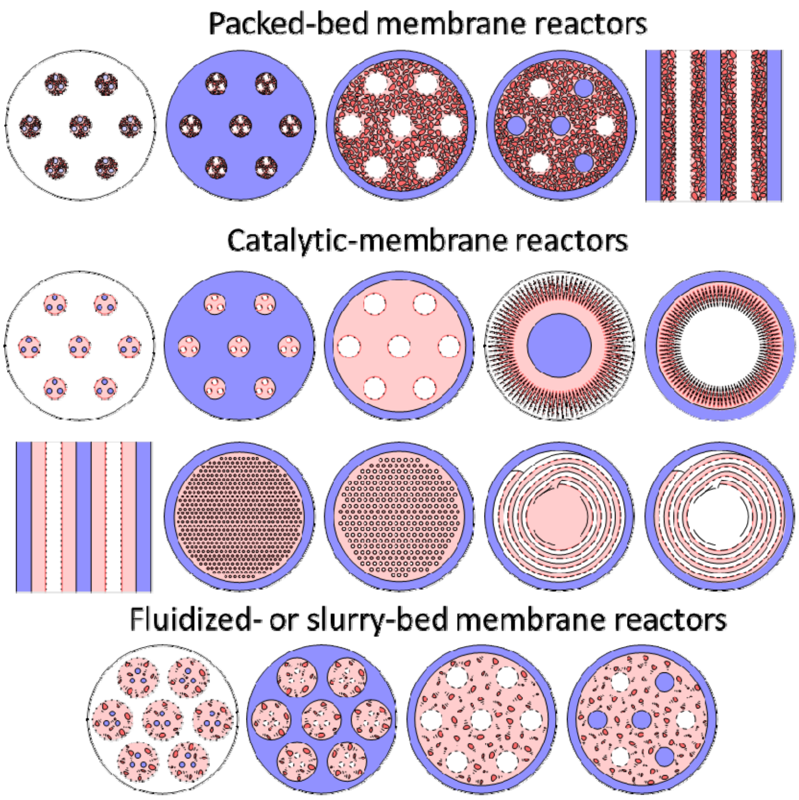


**Figure 3: Membrane reactor types included in the conceptual selection and design methodology developed by PDC**

## 5) Membrane reactor design

The field of membrane reactor design is largely unexplored. The large-scale design of membrane reactors requires a completely different approach from conventional reactors, due to the more complex manifolding, the need to optimize heat and mass transfer and match both the reaction rates for the given catalyst. Scale-up of reactors to multi-tube systems is currently generally a achieved by “numbering-up” of the single-tube system. However, in the longer term this is not the appropriate (cost-effective) way to design a membrane reactor. The CARENA project devoted much effort to this essential aspect.
One of the key activities has been the development of a conceptual selection and design methodology which includes 19 membrane reactor types considered as candidates: packed-bed membrane reactors, catalytic-membrane reactors, fluidized/slurry bed membrane reactors (see Figure 3). Each membrane reactor type is evaluated on 12 criteria and the methodology provides its user with a ranking of membrane reactor types from the most to the least likely candidates. Other tools developed in the CARENA project which are useful in process and reactor design are correlations to estimate state of the art permeation fluxes through membranes commonly applied in membrane reactors as a basis for costing membranes.

For the palladium based membrane reactors, both for reforming and for propane dehydrogenation, much work has been done within the project to design and optimize the membrane reactor and process design. This work included making full-scale designs, experimental validation, detailed modelling and extensive process evaluations. Procedures to estimate the capital and operating costs related to membrane reactors at the conceptual design stage where developed. Capital cost estimation procedures have been constructed by combining membrane cost information and cost correlations for conventional units, most notoriously pressure vessels and heat exchangers.
A completely different and innovative way to integrate membranes and catalyst is to make the functional separation in a layer around a catalyst particle. Very successful work has been done by JM and IRCE Lyon in making catalyst for selective oxidation of CO in a propane/propylene containing mixture using a selective layer surrounding the catalyst.

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| Key Message “Reactor design” | Optimal design of membrane reactors is still an open field. There are no design rules to determine the optimal membrane reactor configuration. For example the extensive work done in the CARENA project illustrates that the choice between the open or closed architecture can only be verified based on extensive evaluation of design parameters, experimental results and costing studies.<br>The use of membranes in the reactive environments invites to explore non-conventional reactor approaches. An example developed in the CARENA project is the use of catalyst covered with selective layers to enhance reaction selectivity. Also the use of structured catalyst in connection with membrane reactors warrants further investigation. |

Publicly available CARENA results on Membrane Reactor Design

**Key Publications**

**University of Salerno**: Palma V., Ricca A. and Ciambelli P., *Monolith and foam catalysts performances in ATR of liquid and gaseous fuels*, Chemical Engineering Journal, 207-208 (2012) 577-586

**University of Salerno**: Palma V., Ricca A. and Ciambelli P., *Structured catalysts for methane autothermal reforming in a compact thermal integrated atr reformer*, Chemical Engineering Transaction, 29 (2012) 1615-1620

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**Technion**: M. Sheintuch, *Criteria for palladium membrane reactor design: architecture, thermal effects and autothermal design*, Book Palladium Membrane Technology for Hydrogen Production, Carbon Capture and Other Applications: Principles, Energy Production and Other Applications.,Ed Elsevier, 2014, P167-189

**CNRS-IRCELyon:** S. Li, C. Aquino, L. Gueudre, A. Tuel, Y. Schuurman,D. Farrusseng,Diffusion-Driven Selectivity in Oxidation of CO in the Presence of Propylene Using Zeolite Nano Shell as Membrane, ACS Catalysis, 2014,4(12),4299-4303

**CARENA reports:**

- CO tolerant Propylene Oxidation Catalyst (JM)
- Final report on costing of membrane reactors (PDC)

## 6) Membrane application and membrane scale-up

Membranes with a good performance are a pre-requisite to bring membrane technology to maturity. However, as the membranes move “out-of-the-lab”, many other different aspects will play a role, including scale-up, development of industrial manufacturing routes, achieving sufficient lifetime and understanding the impact of conditions on the lifetime, etc. Within CARENA important steps in scaling-up included:

- Manufacturing of long (¼ of the expected full scale) dead-end tubular perovskite membranes scalable at industrial scale was developed by StGobain. Tubes delivered to IRCE Lyon for testing showed oxygen flows which correspond to the state-of-the-art.
- Steps were made on membrane development by Pd-sputtering, which is considered as a technology suitable for up-scaling. Much attention was devoted to understanding the factors and parameters determining adhesion of the functional layer to the support for different types of support.
- SOD layers were investigated at LUH. The membranes fabrication was scaled up from the 19 mm disc plate to 15 cm tubes of 1 cm outer diameter. Separation performance of the tubular membrane is only slightly lower than the planar discs.

Membrane fabrication is only one aspect which needs to be developed to make the membranes a mature technology.  Some examples of fields where the CARENA project achieved interesting results contribution to the membrane

- Attractive results were obtained at CNRS IEM in *operando* membrane characterisation, correlating their acoustic signatures with membrane pore sizes, support structure, materials, type of gas, applied pressure and gas transport regimes.Molecular simulations were found to fit experimental data obtained from high frequency acoustic microscopy. It was concluded that combining molecular simulation and acoustic wave properties is an asset to monitor in real time, i.e. *operando*, the evolution of the mechanical properties of porous media and membranes.

- Further understanding of degradation mechanisms in Pd based membranes during operation has been achieved through experimental and computanional modelling activities based on:
  - *In situ* synchrotron-based FTIR experiment on Pd membranes carried out at DIAMOND in simulated PDH conditions. Membranes were supplied by ECN and SINTEF and were prepared by two deposition methods (sputtering and electroless plating) with various compositions (Pd and Pd-Ag) and pre-conditionement
  - Long term testing of Pd membranes in SMR condition at ECN and post characterisation of the membranes.
  - A methodology based on computational modelling developed at Technion for predicting permeance and its inhibition by adsorption competition of propane and propylene.
- An important step to shorten the development cycle for oxygen conducting membranes is a method, based on experiments and modelling, which predicts $O_2$ flux in oxygen transport membranes based on characterization of the powders.

| | |
|---|---|
| Key Message "Membrane Scale-up" | Moving membrane reactors out of the lab and into the real world requires membranes with sufficient performance and lifetime, but also the availability of methods to fabricate full-scale membranes using industrial methods. CARENA has addressed a wide range of issues, including fabrication methods, understanding lifetime and characterization methods, which are important to bring membranes for membrane reactors to a next readiness level. |

Publicly available CARENA results on membrane application

Key Publications

**CNRS-IEM:** E. D. Manga, B. Blasco, P. da-Costa, M. Drobek, A. Ayral, E. le Clezio, G. Despaux, B. Coasne, A. Julbe, Effect of Gas Adsorption on Acoustic Waves Propagation in MFI Zeolite Membrane Materials: an Experimental and Molecular Simulation approach, Langmuir, 2014, 30 (34), 10336–10343 DOI: 10.1021/la502182k

**CNRS-IRCELyon:** M. Rochoux, Y. Guo, Y. Schuurman, D. Farrusseng, *Determination of oxygen adsorption–desorption rates and diffusion rate coefficients in perovskites at different oxygen partial pressures by a microkinetic approach*, Phys. Chem. Chem. Phys., 2015, 17,1469-1481

## Other CARENA Results in the Public Domain

The information in this summary does not include detailed results where information is confidential. However, much of the information which has been generated in the project *is* in the public domain. A list of all publications can be found on the project website (http://www.carenafp7.eu).

## Overall assessment CARENA results

*Bringing membrane reactors closer to industrial reality requires coherent progress in many fields. The CARENA project has shown good progress in these separate fields as well as a major step in developing the multi-disciplinary approach linking these knowledge fields.*

## 4: Potential impact and main dissemination activities and exploitation results

One of the objectives of the CARENA project is to valorise the results in the best possible way. To achieve this, we have created and implemented an **Intellectual Property Rights (IPR) strategy**, composed of the following elements:

- Patent analysis and mapping
- Development of an IPR strategy
- Promoting/facilitating IPR generation
- Promoting/facilitating IPR exploitation

The IPR strategy was positively reviewed by the CARENA Strategic Advisory Board, consisting of external knowledgeable experts in the field of membrane and reactor R&D.
As a means to promote IPR generation and exploitation **22 CARENA innovations of interest were consistently monitored** during the project. Per topic the following elements were addressed:

- Knowledge and results being generated
- Related work package (WP) and task
- Potential application area
- Existing knowledge gaps to make the ideas patentable
- Unicity of the idea and relevant prior art
- Owner, other beneficiaries, and contact person
- Status of IPR and exploitation
- Future initiatives

In total two **patent applications** have been filed prior to CARENA, two patent applications during the project and two patent applications are in preparation.
The CARENA exploitation activities focused on facilitating partners in exploiting results, to broaden exploitation to other applications, and to define user benefits and funding for exploitation. Key tools that were used to realize these objectives are:

- **Workshop 'Catalytic Membrane Reactors, What's Next?'**, organized in Petten, Netherlands, on 29-30 April 2015. In total 54 participants from 9 countries gathered to be informed about the CARENA highlights and innovations, and to discuss about future initiatives related to Catalytic Membrane Reactor technology and processes. Further information about the workshop can be obtained from the CARENA website: http://www.carenafp7.eu/index.php/Past/Past.html#WSPetten2015.
- Development of **Innovation Leaflets**, which offer an excellent opportunity to advertise the CARENA achievements and raise external interest with the objective to valorise IP, attract partners for further development of the technology, or to broaden exploitation of the CARENA results to other applications.

Innovation Leaflets (Figure 1) summarize the technology developed or a specifically needed by CARENA partners to exploit their new technology in full. In total **10 Innovation Leaflets** have been developed in CARENA, as listed in Table 1. The exploitation activities enabled the CARENA partners to establish new contacts and start new initiatives, particularly for future collaborative activities. It is expected that in many cases this is in the form of a continuation of the technology development, but it can also be the exploitation of the technology.

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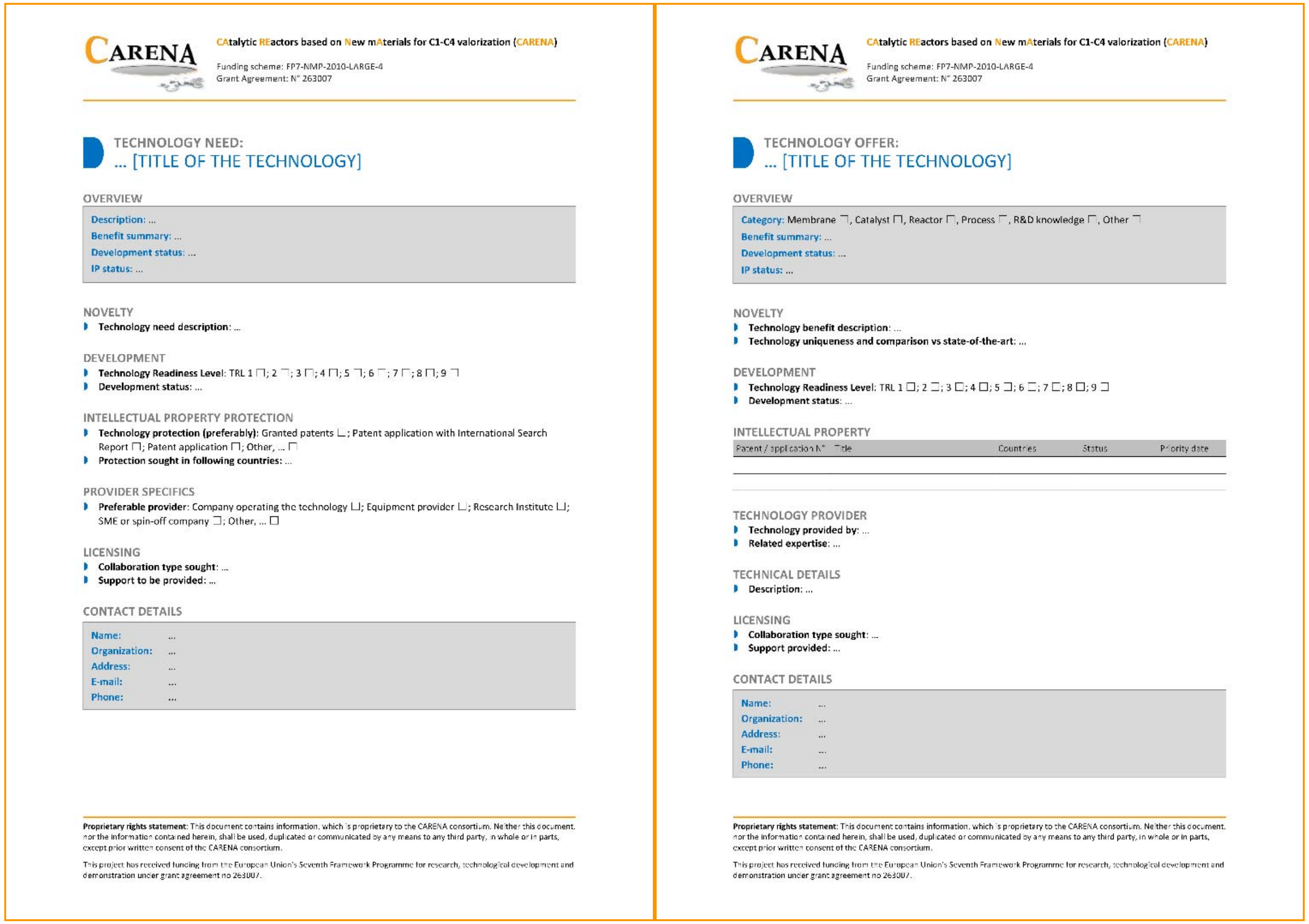
Table 1: CARENA Innovation Leaflets

| No. | Type | Title | Partner |
|---|---|---|---|
| 1 | Technology offer | Size selective catalysis in metal catalysis by molecular sieving in membrane nanoreactor | CNRS-IRC |
| 2 | Technology offer | Prediction of oxygen flux in perovskite type membrane from measurement on powder | CNRS-IRC |
| 3 | Technology offer | Integrated membrane reactor for enhanced methane steam reforming | ECN |
| 4 | Technology offer | Novel metal-organic framework (MOF) membranes for $H_2$ separation | Hannover |
| 5 | Technology offer | Novel zeolite membranes of type SOD fro $H_2O$ separation | Hannover |
| 6 | Technology offer | iPOSS® membranes | UTwente |
| 7 | Technology offer | Membrane based propane dehydrogenation process for propylene production | KT |
| 8 | Technology need | Membranes for coke free removal of $H_2$ from a $C_3H_x$ mixture | KT |
| 9 | Technology offer | Conceptual design methodology for catalytic membrane reactors | PDC |
| 10 | Technology need | Membrane supports for H2 selective Pd membranes manufactured by sputtering | Acktar |

. The Innovation Leaflets were presented as posters and handouts at the workshop ‘Catalytic Membrane Reactors, What’s Next?’ on 29-30 April 2015 and are published on the CARENA public website: http://www.carenafp7.eu/index.php/Follow-up/follow_up.html. The intention is also to post them on other central networks, such as the European Enterprise/Business Network. Furthermore, CARENA partners can use them for their own purposes.

Figure 1: Innovation leaflets templates for Technology Offer and Technology Need



CAtalytic REactors based on New mAterials for C1-C4 valorization (CARENA)

Funding scheme: FP7-NMP-2010-LARGE-4
Grant Agreement: N° 263007

TECHNOLOGY NEED:
... [TITLE OF THE TECHNOLOGY]

OVERVIEW

Description: ...
Benefit summary: ...
Development status: ...
IP status: ...

NOVELTY

- Technology need description: ...

DEVELOPMENT

- Technology Readiness Level: TRL 1 ; 2 ; 3 ; 4 ; 5 ; 6 ; 7 ; 8 ; 9
- Development status: ...

INTELLECTUAL PROPERTY PROTECTION

- Technology protection (preferably): Granted patents ; Patent application with International Search Report ; Patent application ; Other, ...
- Protection sought in following countries: ...

PROVIDER SPECIFICS

- Preferable provider: Company operating the technology ; Equipment provider ; Research Institute ; SME or spin-off company ; Other, ...

LICENSING

- Collaboration type sought: ...
- Support to be provided: ...

CONTACT DETAILS

Name: ...
Organization: ...
Address: ...
E-mail: ...
Phone: ...

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Funding scheme: FP7-NMP-2010-LARGE-4
Grant Agreement: N° 263007

TECHNOLOGY OFFER:
... [TITLE OF THE TECHNOLOGY]

OVERVIEW

Category: Membrane , Catalyst , Reactor , Process , R&D knowledge , Other
Benefit summary: ...
Development status: ...
IP status: ...

NOVELTY

- Technology benefit description: ...
- Technology uniqueness and comparison vs state-of-the-art: ...

DEVELOPMENT

- Technology Readiness Level: TRL 1 ; 2 ; 3 ; 4 ; 5 ; 6 ; 7 ; 8 ; 9
- Development status: ...

INTELLECTUAL PROPERTY

| Patent / application N° | Title | Countries | Status | Priority date |
|---|---|---|---|---|

TECHNOLOGY PROVIDER

- Technology provided by: ...
- Related expertise: ...

TECHNICAL DETAILS

- Description: ...

LICENSING

- Collaboration type sought: ...
- Support provided: ...

CONTACT DETAILS

Name: ...
Organization: ...
Address: ...
E-mail: ...
Phone: ...

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## 5: Address of project public website and relevant contact details

For more information on the project, please refer to the CARENA website (http://www.carenafp7.eu).

*The CARENA project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no* 263007*".*

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For more information see:
**http://carenafp7.eu/**