

# Catalytic Reactors based on New Materials for C1-C4 valorization

Newsletter – Issue 6 – June 2014

# **Editorial**

"Was it difficult to find a theme for the editorial? Of course not! Hard to escape the World Cup mania. And there are so many parallels between the World Cup and a large project! Look at parallels between the CARENA team and winning football teams, look at the discussion on style vs. effectiveness, see how both in projects and world cups sometimes "sure winners" make an early exit and other teams become the surprise of the tournament.

But no, I would like to use the World Cup to bring you an insight of the best Dutch footballer ever: Johan Cruijff. Famous for his elegant football. But today in the Netherlands he is most famous for his unique handling of the Dutch language and most memorable one-liners. To such an extent that in the Dutch language "Cruijffian" is immediately understood to mean something which is the same time completely obvious, obscure and brilliant once you understand what it means. "If you can't win, make sure you don't lose". "If you play for possession, you don't need to defend: there is only one ball". "Don't confuse speed with insight; if I start before the others it just looks as if I am fast". Just to name a few. However, the one which had me thinking about our project, was the following one:

"If you want to play faster, you can run harder, but it's the ball that determines the pace".

To get the ball somewhere quickly, do not run with the ball. It is hard work and you can never beat the speed of passing the ball between the players of the team. It's the basic lesson small kids learning to play football are told again and again, but one of the most difficult to learn. Not only kids, but also grown-ups tend to overlook the importance of passing. As it is in a project such as CARENA. Working hard to ensure you deliver what you promised is necessary and good for the project. But in the end, exchanging the right information between the partners at the right moment is an even more important for the success of the project. Quick passes and frequent exchanges are much more effective. Let the ball determine the pace. We all know it's that simple. Or as Cruijff puts it: "Football is so simple, but playing simple football is very difficult"

Arend De Groot

## What is CARENA ?

The 1<sup>st</sup> of June 2011 marked the start of the **CARENA** project: **Catalytic Reactors based on New Materials for C1-C4 valorization.** It is an 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 will promote the implementation of catalytic membrane reactors in the European chemical industry.

Collaborative Project: Large-scale integrating project FP7-NMP-2010-LARGE-4 48 months - Start day : 1s<sup>t</sup> June 2011





# 1- Review of the Current State

The drizzling weather during the 3<sup>rd</sup> annual meeting on May 26-28<sup>th</sup>, 2014 in Munich was by far not representative for the current state of the CARENA project. Beside the typical formal and status presentations, there were effective cross-work package meetings and 16 interesting highlight presentations from CARENA researchers and developers. This did not only provide a highly interesting meeting program, but also offered an excellent opportunity to take note of the impressive progress and results in the CARENA project over the past year.

In year 3 of the CARENA project major advancements in catalyst, membrane development and process modelling have been reached. Although the available space is too little to highlight all developments and the excellent work done by the CARENA partners, many deserve to be mentioned.

Twente University developed and patented new polyPOSS-imide hybrid membranes, which have improved mechanical and thermal stability compared with conventional polymeric membranes. The permselectivity can be tailored by tuning the POSS cage spacing using different imide linkers and by modifying the affinity groups. ECN and SINTEF shed more light on the mechanism of Pd membrane deactivation and possible measures to reduce coking. With support of CARENA partners Acktar improved the sputtered Pd membranes. In the area of membrane characterization Diamond successfully performed in-situ X-ray synchrotron measurements, while IEM developed an Acoustic Emission (AE) technique for in-situ characterization of membranes.

Many catalyst developments were achieved by Johnson Matthey, who made advancements in the development of catalysts and coatings for a high number of applications, including propylene oxidation, oxidative coupling of methane and selective CO oxidation. Catalyst were developed and tested by IRCE-Lyon in a number of experimental setups developed under CARENA. The development of yolk-shell catalysts for selective oxidation needs to be mentioned in that respect. University of Salerno made good progress on how to improve the performance of steam reforming and propane dehydrogenation catalyst.

The understanding of catalytic membrane reactors and their implementation in chemical processes advanced by modelling work. CNRS-IRC in Lyon developed a micro-kinetic model for Oxygen Transfer Membranes (OTM). PDC made significant progress with the development of conceptual design methodology of catalytic membrane reactors. Process models were developed for the steam methane reforming, MTM and OCM process, and propane to acrylic acid.

Of course, R&D does not proceed smoothly in every aspect. Bottlenecks were encountered, for which alternative or backup solutions had to be defined.

Main driver for the last CARENA year is to integrate all the valuable results in real catalytic membrane reactors. It is like the Strategic Advisory Board stressed: CARENA will finally be judged on the Catalystic Membrane Reactor development it achieved!

The outlook is good. Dissemination and exploitation proceed well with 19 papers, 22 oral presentations and 20 poster presentations. One patent has been filed and quite a number of applications are in preparation. Collaboration between partners goes smoothly and there are no big issues in project management to report. The last year faces many technical challenges, but it promises to become a very productive final year for the CARENA project.





## 2 – Dissemination : PhD Defense

Our first ESR, Antonio Ricca, from the University of Salerno has successfully defended his thesis on 14 April 2014. Congratulations and all the best for the future



# Antonio Ricca

# Department of Chemical and Food Engineering

Ph.D. Course in Chemical Engineering (XII Cycle-New Series)

# INNOVATIVE CATALYSTS FOR PROCESS INTENSIFICATION OF METHANE REFORMING AND PROPANE DEHYDROGENATION REACTIONS

Supervisor : Scientific Referees :

Prof. Vincenzo Palma Prof. Vincenzo Palma Prof. Paolo Ciambelli Ing. Gaetano Iaquaniello PhD. Course Coordinator : Prof. Paolo Ciambelli





### 3 – Interview with a CARENA partner

I hold a BSc degree from the Technion and a PhD degree from University of Illinois. Between the two I worked for a brief period for the government as an Environmental Eng. When I searched for a PhD advisor at U of I, I looked for an environmental project, and was offered a topic on "Oscillations during catalytic CO oxidation". That turned out to be a great topic even though it had little to do with environmental technology: It was a novel topic, it introduced me to non-linear dynamics- an emerging field at the time, and to reaction engineering. Most of my research in subsequent years was devoted to dynamics of catalytic reactors, unveiling new behaviors like chaos, pattern formation, using new mathematical tools like bifurcation theory and discussing their implications.

My environmental eng. education, led me to the area of catalytic abatement of water pollutants, and to realize it may have great technological potential. We have developed two catalytic processes, removal of nitrates by hydrodenitrification (currently in its 2<sup>nd</sup> year as an incubator project, see http://welltodo.co.il/index.html) and catalytic regeneration of activated carbon.

My interest in membrane reactors emerged when I spend a summer in Mobil Central Research Lab. in Princeton NJ. I studied the DH of isobutane and of propane in a self-supported Pd/Rh membrane reactor. The former went well but the latter led to fast deactivation.

#### What is the added-value of an EU project such as CARENA compared with other partnerships on the same topic you may be involved in?

Building a MR requires at least three elements: catalyst, membrane and a reactor. Working in a group that has the expertise in these three elements allow you to check new ideas by modification of one or several elements. In previous studies of carbon membrane reactor for isobuatne DH and of autothermal methane steam reforming we purchased the catalysts and the membranes and had to accommodate the reactor design. In CARENA we see emerging efforts of modifying the membrane and catalyst to overcome reaction shortcomings (coking).

#### CARENA brings together Research labs and industry. How do you view research-industry collaboration within the framework of the project?

Such collaboration is great as it allows you to compare various solutions: While previously we worked with one manufacturer of Pd (or Pd/M) membrane, now we are in contact with four (including Sintef, ECN, Acktar). The other aspect is the hope to modify the catalyst and membrane as described above.



Read the full interview online https://www.carenafp7.eu/index.php/Interviews/Interviews.html

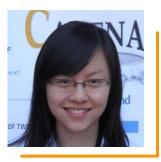


Moshe Sheintuch Technion. Israel



4 – Interviews with ESR/ER





Schiwen Li is an ESR at the Institute for Research on Catalysis and Environment (IRCELyon) in Lyon, France under the direction of Dr. David Farrusseng.

Nanyi Wang is an ESR at Leibniz University of Hannover in Germany under the direction of Prof. Juergen Caro.

#### Do you have some advice to master/engineer students considering taking a PhD?

Think about whether you are really eager to take a PhD or not.

If yes, then choose a subject which you are really interested in, because this can give you endless energy in the following years!

Before the start of a PhD, you must consider about your passion of the research, choose a subject which you are interested in, and be physically and mentally ready for hard working and high pressure.

#### What are your plans after completing the PhD?

I would like to continue the work in the area of materials and catalysis, especially, in the development and application of novel catalysts. Personally, I prefer to work in industry, because the application of catalysts in industry is the most attracting part for me at this moment!

So far I have decided to try to find a job in a company in Germany, to see if my research capacity can make contribution to industry.

Thank you Schiwen & Nanyi for giving us a glimpse into your progress with research activities!

Read the full interviews online







## 5 – Upcoming Events



## Next joint CARENA, CoMETHy, DEMCAMER, RE4CELL & NEW-JU Workhop Scale-up of Pd Membrane Technology From Fundamental Understanding to Pilot Demonstration

### 20-21 November 2014. The Netherlands

This event will be organized in the frame of 4 FP7 European projects: **CARENA, COMETHY, DEMCAMER and RE4CELL** working and developing palladium membrane technology for hydrogen production. A 2-days event including a visit to ECN.

The current workshop is the follow-up of the first "Pd-membrane Scale-Up" workshop as held in Rome, Italy in November 2012. It proved a unique knowledge-sharing experience for both the EU-funded organizing projects and all participants, providing a clear picture of the status of Pd membrane technology in view of its commercialization.

The workshop covers a good breadth of topics that are critical for Pd membrane technology scale-up: from the fundamentals of Pd membranes, support & seal manufacturing, to various concepts of membrane module design & system integration; from lab-scale long-term stability testing results to industrial pilot plant operational insights. The event brings together representatives of academia, research institutions and industrial stakeholders, and will form a unique knowledge sharing experience for all participants.

**Registration**: The following link can be used for registration for the workshop: <u>https://www.ecn.nl/registration/PdMembraneWorkshop/</u> Deadline : 17 October 2014

The workshop is free of charge; travel and accommodation at own expense



## Next 12th International Conference on Catalysis in Membrane Reactors -ICCMR12-Poland

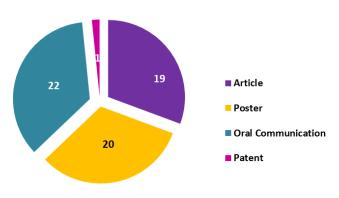
> Involvement in the preparation.>> Special session devoted to research projects



## 6 – Publications // June 2011- May 2014

The PhDs and senior researchers are active and participate to several national and international conferences and meetings in order to communicate the CARENA's results. They have reported several scientific publications in peer-reviewed journals.

Please find more details via this link : <u>http://www.carenafp7.eu/index.php/Publications/P</u> <u>ublications.html</u>



# Miscellaneous

13th International Conference on Inorganic Membranes, ICIM, Brisbane (Australia), 6-9 July 2014 <u>http://www.icimconference.com</u> International Conference on Membranes, ICOM Suzhou (China), 20-25 July 2014 <u>http://icom2014.org</u>

Dr. Arend DE GROOT (Coordinator) ECN – The Netherlands Email: <u>a.degroot@ecn.nl</u>

Dr. Hank VLEEMING (Operational Manager) PDC – The Netherlands Email: vleeming@process-design-center.com Prof. Gilbert RIOS (Public Dissemination Manager)

EMH – Belgium Email : <u>Gilbert.Rios@univ-montp2.fr</u>

Dr. Sadika GUEDIDI (Dissemination Officer) EMH –UM2– France Email: Sadika.Guedidi@univ-montp2.fr

Disclaimer:

The present document reflects only the author's views and the European Union is not liable for any use that may be made of the information contained therein.