Advanced Multi-Fuel
Reformer for Fuel CELL
CHP Systems

ReforCELL

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Summary

REforCELL aims at developing a high efficient heat and power cogeneration system based on:

i) design, construction and testing of an advanced reformer for pure hydrogen production with optimization of all the components of the reformer (catalyst, membranes, heat management etc) and

ii) the design and optimization of all the components for the connection of the membrane reformer to the fuel cell stack.

The main idea of REforCELL is to develop a novel more efficient and cheaper multi-fuel membrane reformer for pure hydrogen production in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit.
Traditional concept

Layout of PEM m-CHP unit using traditional reforming (TR) for fuel processing
ReforCELL concept

Layout of PEM m-CHP unit using membrane reformer (MR) for fuel processing
This research is carried out by a multidisciplinary and complementary team consisting of 11 top level European organisations from 6 countries: 6 Research Institutes and Universities working together with representative 5 top industries in different sectors (from hydrogen production to catalyst developments to boilers etc.).
Consortium

1 TECNALIA, Spain
2 TU/e, Netherlands
3 CEA, France
4 POLIMI, Italy
5 SINTEF, Norway
6 ICI, Italy
7 HYGGEAR, Netherlands
8 SOPRANO, France
9 HYBRID, Netherlands
10 QUANTIS, Switzerland
11 JRC, Netherlands
Project objectives

- Development of novel catalysts
- Development of high performance Pd-based membranes
- Novel catalytic membrane reactors
- Prototype reactor testing and validation
- BoP optimization
- Novel micro-CHP system
- Modelling and simulation of both reactors and complete system
- Life Cycle Analysis, industrial risk assessment study
Work Structure

WP2. Industrial specifications of FC micro-CHP [ICI]

WP3. Catalysts development [HYBRID]
- Catalyst preparation
- Catalyst characterisation
- Activity test

WP4. Membrane development [SINTEF]
- Material for membranes
- Membranes development and characterization

WP5. Lab scale reactors [TU/e]
- Integration in micro-structured membrane reactors
- Testing and model validation

WP6. Novel ATR prototype [HYGEAR]
- Design of Pilot
- Set up and testing
- FAT
- Testing and validation
- Process design & Simulation

WP7. Integration and validation of micro-CHP system [ICI]
- Fuel Cell stack selection
- FC - CHP system optimization
- Integration and testing

WP8. LCA and Safety analysis [QUANTIS]

WP9. Dissemination and Exploitation [HYGEAR]

WP1. Management [TECNALIA]
Industrial reforming

Auto-thermal reforming (ATR)

\[ \text{dry reforming} \quad 2 \text{CH}_4 + \text{O}_2 + \text{CO}_2 \leftrightarrow 3 \text{H}_2 + 3 \text{CO} + \text{H}_2\text{O} \]

\[ \text{Steam methane reforming (SMR)} \quad 4 \text{CH}_4 + \text{O}_2 + 2 \text{H}_2\text{O} \leftrightarrow 10 \text{H}_2 + 4 \text{CO} \]

- Industrially reactions are performed over nickel based catalysts
- Typical loading lies in the range of 20-50 wt % depending on the type of catalyst (e.g. SMR, ATR)
- High reaction temperature (800 – 1100 °C) is maintained to prevent coking of the catalyst
Low temperature catalyst

- Platinum group metals catalyze reforming reactions at lower temperature with less formation of coke
- Rhodium, Ruthenium and Platinum show reasonable to good activity
- Ceria zirconia support increases the catalyst effectivity

![Diagram of low temperature catalyst with Ru, Rh, Pd, Os, Ir, Pt]

- Good activity
- Less expensive
- Sensitive to high T

- Good activity
- €€€
- Tested at TU/e

- Extremely toxic
- Volatile

- Less active

- Active
- Expected to have good coke resistance

29/01/2016 / Pág. 11 (Disclosure or reproduction without prior permission of ReforCELL is prohibited).
Reforcell reforming

- Ruthenium catalyst dispersed over a ceria/zirconia support
- Operation in fluidized bed to prevent temperature problems
- Mechanical and chemically stable
- Synthesis scaled up to kilogram scale
Membranes Development

- Selection of ceramic and metallic porous material for membrane supports
- Development of ceramic interdiffusion layer for metallic support
- Development and optimization of Pd-based membranes for H$_2$ separation
- Development and optimization of non-Pd based for hydrogen separation
- Membrane characterization under realistic reforming conditions in lab-scale units prior to application of the optimal membranes in the pilot prototypes
- Manufacturing of dense-metal membranes for integration into prototype unit
- Analysis of production costs and scale up of the membrane production technology unit
METALLIC SUPPORTED Pd MEMBRANES


- ~4.5 µm thick Pd-Ag membrane
- Membrane length: ~14 cm
Long-term stability test

Metallic supported membrane M14. Long-term stability test over time at 400 °C

Membrane M17-E94. Long-term stability test (500-600 °C)

http://dx.doi.org/10.1016/j.ijhydene.2015.10.094
SMR-MR

http://dx.doi.org/10.1016/j.ijhydene.2015.10.094

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http://dx.doi.org/10.1016/j.ijhydene.2015.10.094
SINTEF has improved the pressure and temperature stability of Pd-membranes integrated into micro-channel reactors. Porous stainless steel permeate support increases the temperature stability to 15 bars at 450ºC using a 10 micron thick Pd-alloy.

Two different intermetal diffusion barrier layers, YSZ and TiNₓ, have been deposited using reactive magnetron sputtering and an increase in operating temperature have been obtained. Work is ongoing.

Up-scaling of the micro-channel reactor is ongoing.
Lab Scale ATR-CMR fuel reforming

- Selection of ATR-CMR components: catalysts, membranes and supports, and sealing based.

- Integration of these elements in lab scale reactors specifically designed for ATR.

- Validation of the lab scale reactors performances and identification of the best design for prototype pilot in WP6
Microstructured membrane modules minimize concentration polarisation

- Potentially a very large membrane surface area per catalyst volume (ca. $10^3 - 10^6$ m$^{-1}$)

Stability of microstructured membrane modules

- **Microchannel-supported**
  - Settling of the film into the permeate section
  - Large microstructural changes and porosity formation on feed side
  - Operation limited to 400 °C and 5 bars

- **Porous stainless steel-supported**
  - Fully stable up to 15 bars and 450 °C
  - H₂ flux of 195.3 mL·cm⁻²·min⁻¹ - $P$ of $3.4 \cdot 10^{-8}$ mol·m⁻¹·s⁻¹·Pa⁻⁰·⁵ (5 bar feed pressure)
  - H₂/N₂ permselectivity > 39,000

Integrated membrane reformer

- **Packed-bed membrane-integrated reactor**
  - Ru/\(\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\) reforming catalyst (Hybrid Catalysis, sieve fraction 125-250 µm)
  - Membrane area \(~12.5\ \text{cm}^2\); membrane surface area per catalyst volume of ca. \(10^3\)

- **Membrane reformer experiments**
  - \(T = 550\ \degree\text{C} \quad P = 6\ \text{bars};\ \text{N}_2:\text{CH}_4:\text{H}_2\text{O} = 20:20:60\)

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Lab Scale ATR-CMR fuel reforming

Figure 1 Lab scale FBMR, developed by TU/e

Typical results of ATR at 600 C
Lab Scale ATR-CMR fuel reforming

Membrane bundle ready for tests

CO effect at 600 °C and 2.0 bar

Hydrogen separation tests

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Pilot Scale ATR reactor

**Specifications:**

- Maximum $H_2$ output 5 Nm$^3$/h
- Nominal CHP operation $\approx$ 3.7 Nm$^3$/h
- Partial loads 30 %
- Maximum temperature 600 ºC
- Fluidized bed
- 7 bar$_g$ reaction
- 300 mbar$_a$ hydrogen

H$_2$ outlet
Catalyst inlet
Pd/Ag membrane
Steam
Air
NG inlet
Pilot Scale ATR reactor

- Fuel processor & BOP assembled
- Skid mounted for transportation
- Controlled by PLC
- HMI for fine tuning of parameters and local operation
- Optional control and diagnosis through remote connection
Integration & Validation in CHP-System

- Selection and test of fuel cell stack: definition of a PEMFC stack adapted to the micro-CHP system,
- Optimization of the fuel cell CHP focusing both on technical and economic point of view (example of optimization parameters: feed pressure, permeate side configuration, S/C ratio, etc.)
- Manufacturing and testing of a PEMFC micro-CHP system
ReforCELL: layout of CHP with MR

Layout with sweep gas
ReforCELL: layout of CHP with MR

Layout with vacuum pump
Results: Case studies comparison

Area

![Graph showing electric efficiency vs membrane area for different temperatures and S/C ratios. The graph includes data points for 600 °C, 575 °C, and 550 °C. Notable points include S/C 2.5 and S/C 3.0 at different pressures.]
## Results: Power balances and Efficiency

<table>
<thead>
<tr>
<th>Results</th>
<th>units</th>
<th>Sweep</th>
<th>Vacuum pump</th>
</tr>
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<tbody>
<tr>
<td>S/C after oxidation</td>
<td>-</td>
<td>2.5</td>
<td>3</td>
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<tr>
<td>Pressure reaction side</td>
<td>bar</td>
<td>8</td>
<td>8</td>
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<tr>
<td>Pressure permeate side</td>
<td>bar</td>
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<td>S/C ratio at inlet of ATR-MR</td>
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<td>1.44</td>
<td>1.81</td>
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<td>NG power input [LHV base]</td>
<td>kW</td>
<td>12.50</td>
<td>13.05</td>
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<tr>
<td>Net AC power output</td>
<td>kW</td>
<td>5.00</td>
<td>5.00</td>
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<tr>
<td>Fuel Cell AC power output</td>
<td>kW</td>
<td>6.31</td>
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<td>NG compressor</td>
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<tr>
<td>Air compressor</td>
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<td>0.37</td>
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<tr>
<td>Cathode air blower</td>
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<td>0.19</td>
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<tr>
<td>Vacuum pump</td>
<td>kW</td>
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<tr>
<td>Balance of plant</td>
<td>kW</td>
<td>0.64</td>
<td>0.65</td>
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<tr>
<td>Thermal recovery</td>
<td>kW</td>
<td>6.49</td>
<td>6.77</td>
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<tr>
<td>Net electric efficiency [LHV base]</td>
<td>%(_{\text{LHV}})</td>
<td>40.02</td>
<td>38.32</td>
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<tr>
<td>Net thermal efficiency</td>
<td>%(_{\text{LHV}})</td>
<td>51.97</td>
<td>51.86</td>
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<td>Total efficiency [LHV base]</td>
<td>%(_{\text{LHV}})</td>
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<td>90.18</td>
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<tr>
<td>Total membrane area</td>
<td>m(^2)</td>
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<td>Hydrogen permeation</td>
<td>Nm(^3)/h</td>
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<tr>
<td>Hydrogen Recovery Factor</td>
<td>%</td>
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<td>Avg. driving force</td>
<td>mbar(^{0.5})</td>
<td>7.03</td>
<td>10.46</td>
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Final dissemination and exploitation workshop

Save the date!

Final dissemination and exploitation workshop

11/12/2015 at Grenoble, France at CEA-LITEN

Dear Colleagues,

The project ReorCELL is coming to its final days after years of development and interesting findings. The long journey was very exciting and led to the manufacturing of the pilot system of a PEM based mCHP using ATR membrane reactor for production of hydrogen.

We would like to share some steps of our journey by inviting you to our final dissemination and exploitation event to be held at the facilities of CEA-LITEN.

Other projects with technologies related to those developed in ReorCELL will present their findings giving the workshop a broad overview of membrane based hydrogen production and CHP technologies.

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Life Cycle Assessment and Safety Issues

Global environmental assessment of the new technologies:

- Environmental Life Cycle Assessment analysis of the CMR-CHP system.
- Identification and evaluation of key safety parameters and risk analysis
- Proposal of recommendations for the safe operation of the CMR-CHP technology.
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Thank you for your attention

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