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## Multi-fuelled solar steam reforming for pure hydrogen production using solar salts as heat transfer fluid

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### Abstract

This paper presents a project named CoMETHy (Compact Multifuel-Energy to Hydrogen converter) co-funded by the European Commission under the Fuel Cells and Hydrogen Joint Undertaking (FCH JU). The project is developing an innovative steam reformer for pure hydrogen production to be powered by Concentrating Solar Power (CSP) plants using molten salts as heat transfer fluid. Due to the limitations in the molten salts maximum operating temperature of 550°C, the reformer should operate at lower temperatures than conventional steam reforming processes. This implies the development of an innovative system, involving different R&D topics presented in this paper.

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**Keywords:** hydrogen production, steam reforming, solar reformer, membrane reactor, molten salts;

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**Nomenclature**

CoMETHy	Compact Multifuel-Energy to Hydrogen converter
CSP	Concentrating Solar Power
ESR	Ethanol Steam Reforming
FC	Fuel Cells
FCH JU	Fuel Cells and Hydrogen Joint Undertaking
GHG	Greenhouse Gas
GHSV	Gas Hourly Space Velocity
LPG	Liquefied Petroleum Gas
MS	Molten Salts
NG	Natural Gas
RDF	Refuse Derived Fuel
R&D	Research and Development
S/C	Steam-to-Carbon ratio
SiC	Silicon Carbide
SMR	Steam Methane Reforming
WGS	Water-Gas-Shift reaction

**1. Introduction**

The application of solar-thermal power to directly drive heat demanding thermochemical conversion is one of the most rational ways to exploit solar energy. This approach enhances the reduction of carbon footprint of chemical conversion, and allows the chemical storage of solar energy. Particularly, in fuel refinery it is possible to improve the heating value and the environmental impact (i.e. the overall “quality”) of the primary feedstock by the aid of solar energy: in this case the final product, often called “solar fuel”, will partially or totally drive solar energy in its chemical energy.

Additionally, the worldwide hydrogen demand is increasing, and its use in Fuel Cells (FCs) is expected to make hydrogen one of the foremost fuels in a future more sustainable energy system, mainly thanks to its low environmental impact when used in FC systems.

On the other hand, the extensive introduction of hydrogen as energy vector is limited by the actual lack (and costs) of a reliable hydrogen distribution infrastructure. This barrier can be surmounted by the development of systems for decentralized hydrogen production (i.e. close to the end-user). Fuel-flexibility and the possibility to power the process with renewable energy sources (solar and/or biomass) are two additional preconditions for sustainable hydrogen production.

The above considerations are on the basis of the project CoMETHy (Compact Multifuel-Energy to Hydrogen converter) co-funded by the European Commission under the Fuel Cells and Hydrogen Joint Undertaking (FCH JU). Indeed, CoMETHy’s general objective is to support the intensification of hydrogen production processes, by developing an innovative compact solar steam reformer to convert reformable fuels (methane, ethanol, etc.) to pure hydrogen, according to the following general reaction scheme:



where  $\text{C}_n\text{H}_{2n+2}$  is the hydrocarbon feedstock that can be even replaced by an oxygenated chemical like ethanol or glycerol.

In case of unavailability of the solar radiation, the reformer should be adaptable to other back up fuels (e.g. natural gas, biomass), depending on the locally available energy mix, in order to keep the desired hydrogen production rate.

## 2. General process description

A general concept scheme is shown in Fig. 1.

In principle, the process under development is based on low-T steam reforming. Process heat is supplied by means of a low-cost and environmentally friendly liquid heat transfer fluid, i.e. the binary Molten Salts (MS) mixture  $\text{NaNO}_3/\text{KNO}_3$  (60/40 w/w), often referred as “solar salt”. This allows coupling with Concentrating Solar Power (CSP) plants using this molten salts mixture as thermal storage system at temperatures up to  $550^\circ\text{C}$ . Accordingly, this fluid collects heat from the different available heat sources and transfers it to the thermochemical plant. A suitable heat storage system, based on the use of the solar salt mixture, allows mismatch between the fluctuating solar source and the often steady running chemical plant: in principle, this makes possible to drive the thermochemical plant at steady state, regardless of the effective instantaneous availability of the solar radiation, even overnight and during cloudy periods of time. Clearly, for a given location of the plant (i.e. given yearly solar radiation characteristics), there is an interplay between the nominal power of the CSP plant (i.e. the solar field area), the heat storage capacity and the amount of back up fuel to balance the solar radiation lacks: this is on the bases of CSP plant hybridization, which can be either achieved by a biomass (or RDF, Refuse Derived Fuel) or fossil fuel (e.g. off-gas) combustor and a best compromise between the CSP and the back-up fuel duties should be identified for the technical-economical optimization of the process [1,2]. Selective membranes allow recovery of high-grade hydrogen and increase conversion despite the relatively low operating temperatures.

If compared to a typical steam reforming process, this steam reforming technology operates at lower temperatures, from typical  $850\text{--}950^\circ\text{C}$  down to  $400\text{--}550^\circ\text{C}$ , with consequent significant gain in material costs since no special steel alloys for high-temperature operation are required. The high-temperature furnace is then replaced by a flameless heat exchanger heated by a liquid molten salts stream, making the whole reactor envelope more compact. Additionally, by operating at lower temperatures, it is possible to combine steam reforming and water-gas-shift (WGS) reactions into a single stage at  $400\text{--}550^\circ\text{C}$ , resulting into a low outlet CO content ( $<10\%$  vol) and a reduction of the reformer heat duty. The integration with membranes avoids dedicated hydrogen separation and purification units, to further improve the compactness and enhance the conversion despite the thermodynamic limitations of low-temperature reforming.

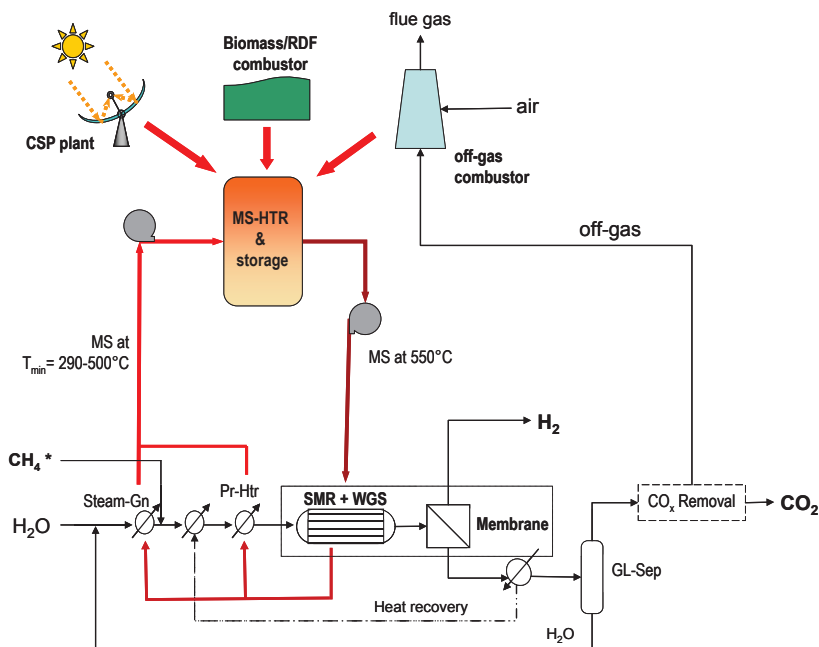


Fig. 1. CoMETHy process concept scheme. MS: Molten Salts. \*supplementary feed: bioethanol or other reformable feedstock (e.g. glycerol, LPG, etc.).

When the thermochemical plant is powered by solar heat, in principle, there will be no combustion in the whole process, and no combustion generated CO<sub>2</sub>-containing flue gases emitted to the atmosphere: this will result in reduction of fuel consumption and greenhouse gas (GHG) emissions being in the order of 40% to more than 50% compared to the conventional route [3].

The reduction of fossil fuel consumption will make the hydrogen production cost less sensitive to the fossil (e.g. NG) price in the solar steam reforming: therefore a breakeven point for the hydrogen production cost is foreseen, resulting in a solar route economically more convenient than the fossil based one [4]. The same solar steam reforming process applied to biomass derived fuels (i.e. bio-fuels like biogas, bioethanol, etc.) allows totally renewable hydrogen production.

An additional advantage of the use of molten salts as heat transfer fluid for steam reforming is when some stand-by periods of the plant are foreseen, as it is the case of small-medium scale reformers for hydrogen refueling stations. In this case, the continuous molten salts recirculation eases the overall process management by maintaining all plant components (e.g. catalyst, membrane) at working temperature (400-550°C) also during stand-by periods using: this minimized start-up periods and ageing due to thermal cycling.

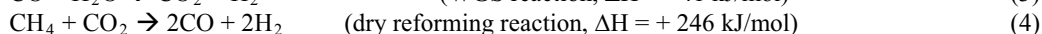
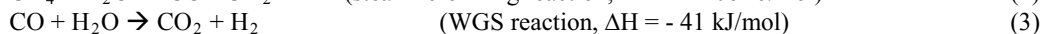
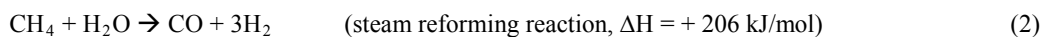
The development of this technology, however, involves a number of interconnected R&D challenges to be faced. Three reference feedstocks have been chosen in the perspective of the multi-fuel application: methane-rich gas (e.g. natural gas), CH<sub>4</sub>/CO<sub>2</sub> mixtures (up to 50%vol. CO<sub>2</sub>, representing biogas), and bioethanol (i.e. diluted ethanol). First, it is necessary to identify and develop suitable catalysts and membranes for this application. Second, the catalyst and the membrane will be integrated in the design of a molten salts heated steam reformer. Finally, the best strategies to couple this reformer with a CSP plant will be studied. These topics are overviewed in the following sections.

### 3. Catalysts for low-temperature solar salt aided steam reforming

#### 3.1. Catalytic materials

Specific catalyst formulations are being proposed, developed and characterized for the steam reforming of the three reference feedstock: pure methane, CH<sub>4</sub>/CO<sub>2</sub> (1:1) mixtures to simulate a biogas, and ethanol.

In the case of methane (and simulated biogas), the following most important reactions take place:



The catalytic activity is first evaluated in the operational range of 400-550°C and 1-10 bar. The effectiveness of the WGS reaction is evaluated too, measured by the final CO content in the outlet stream. Afterwards, the catalyst stability is evaluated in long duration tests (up to 250 hours-on-stream).

Extensive studies led to the identification of promising catalyst materials suitable (in terms of activity, selectivity and durability) for the low-temperature steam reforming of methane (biogas) and ethanol. Carbon formation issues are addressed too. Four catalyst formulations have been selected and characterized, all based on Ni, Pt, Rh as active principle supported on CeO<sub>2</sub> or mixed Ce/Zr/La oxides. These materials, generally in-house synthesized by wet impregnation/precipitation methods, showed satisfactory catalytic activity and stability towards either pure methane or a “simulated biogas” steam reforming, under the “low-temperature” steam reforming conditions foreseen in CoMETHy reactor. The selected catalysts also promote the WGS reaction, leading a product with less than 5%vol. of CO. Also a catalyst effective for both ethanol and methane (or biogas) steam reforming has been identified in the perspective of a “multi-fuelled” steam reforming.

As an example, Fig. 2 depicts the experimental points obtained over Ni/CeO<sub>x</sub> catalyst with a “simulated” biogas (CH<sub>4</sub>:CO<sub>2</sub> = 1:1 v/v) steam reforming at 400-550°C and 1 atm, steam-to-carbon S/C = 3 (H<sub>2</sub>O:CH<sub>4</sub> v/v) compared with the thermodynamic equilibrium curves, with relatively low outlet CO concentration (< 5 %vol. on dry basis).

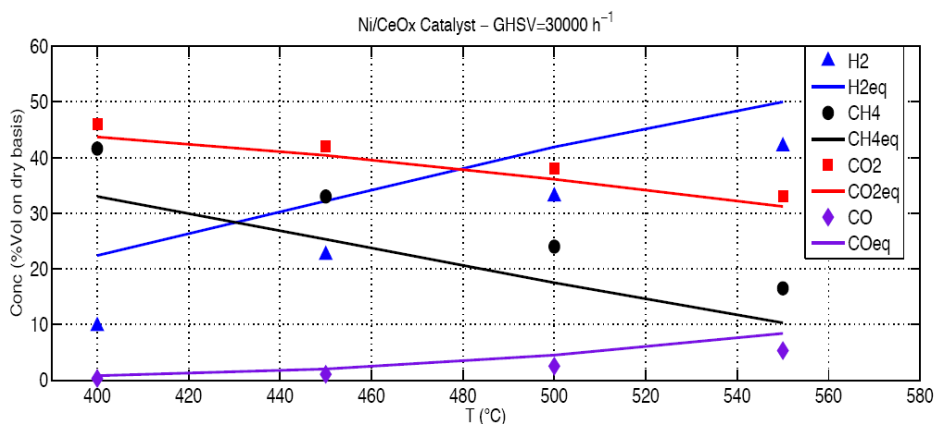


Fig. 2. Comparison between outlet gas composition (dry basis) obtained in steam reforming of a “simulated” biogas (CH<sub>4</sub>:CO<sub>2</sub> = 1:1 v/v) and thermodynamic equilibrium. Catalyst: Ni (10 %wt.)/CeO<sub>2</sub>, 250-355 μm pellets. Operating conditions: 400-550°C, 1 atm, S/C = 3.0, Gas Hourly Space Velocity (GHSV) = 30,000 h<sup>-1</sup>.

In the perspective of a multi-fuel application, ethanol steam reforming (ESR) catalysts are studied too:



Raw bioethanol is available quite diluted and its concentration is energy intensive; on the other hand, the water content in raw bioethanol is favorable for the direct vaporization and subsequent reforming of the water/ethanol mixture. Here stands the interest towards ESR: raw bioethanol can seasonally replace or integrate the gas feedstock if a fuel-flexible system is developed. For this reason, besides activity and stability, selected low-temperature SR catalysts are also evaluated in terms of “fuel-flexibility”, i.e. their capability to operate with different feedstock like methane and ethanol.

Differently from CH<sub>4</sub> reforming, ESR at low-temperature is not much limited by thermodynamics (reasonable ethanol conversions can be obtained even at 500°C) but selectivity towards hydrogen production is an issue. Therefore, the choice of a suitable catalyst is crucial, and bimetallic systems (e.g. Pt(3%)-Ni(10%)/CeO<sub>2</sub>) seem a good choice according to preliminary results.

### 3.2. Structured catalyst supports

The developed catalytic materials need to be carried on suitable mechanical supports which should be characterized by the following features representing essential requirements for an efficient membrane-aided “low-temperature” steam reformer:

1. Enhancement of heat transfer from the reactor wall to the reaction sites. Indeed, steam reforming is a highly endothermic process, so that promotion of heat transfer is a must especially in such “low-temperature” process, where the maximum temperature of the heat source is limited to 550°C. Therefore, large thermal gradients are not acceptable in this case, otherwise the thermal burden would drop the reactor efficiency, and an efficient mean to provide the reaction heat needs to be identified.
2. Minimization of the pressure drop. In the perspective of integration in a membrane reactor, working pressure should be controlled in order to sustain the hydrogen partial pressure for permeation.

Structured open foam ceramic monoliths can be an option to satisfy the above requirements [5]. Two different materials are considered: alumina and silicon carbide. The former is the more conventional ceramic material for catalyst support, the latter is a ceramic with good thermal conductivity. The effect of the structure characteristics like cell sizes (10-45 ppi), void fraction and porosity (80, 85, 90%) has been investigated with a specific experimental campaign, aimed at the evaluation of the heat transfer properties and pressure drop. Three developed SiC samples

with different porosity are shown in Fig. 3. The options for the best fitting of the ceramic foams in the reactor is also studied.

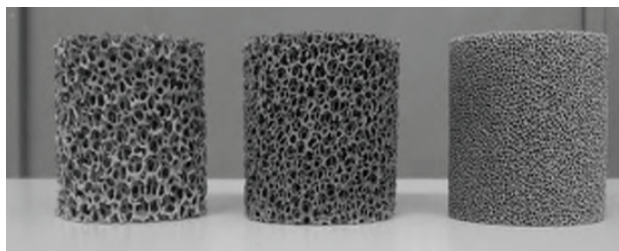


Fig. 3. SiC-made ceramic open foam samples for catalyst support.

A silicon carbide foam with low porosity was finally selected and its heat transfer properties determined.

The selected catalytic material is then coated on the selected ceramic structures and the overall catalytic system performance will be evaluated. To this regard, coating procedures to support the selected active catalytic materials on the selected open foam structures have been developed, including the washcoat deposition and catalyst impregnation. The performances of the as-produced catalyst/support system have been evaluated both in dedicated catalytic tests (mainly focussed on the durability) and in lab-scale integrated membrane reactors. In Fig. 4 is represented a catalysed open foam sample, with a microscopic image of the catalytic layer coated on the ceramic support.

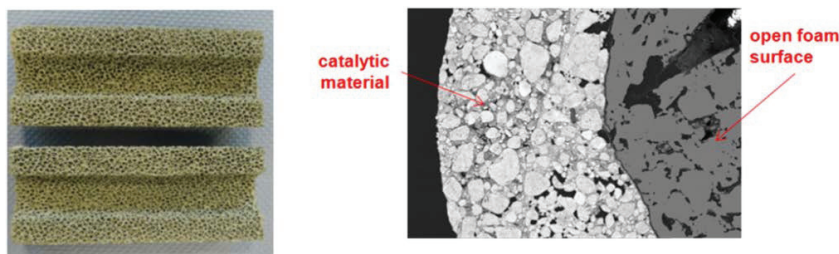


Fig. 4. Example of catalysed ceramic foam developed in CoMETHy.

#### 4. Membranes for low-temperature solar salt aided steam reforming

In parallel with the development of the catalyst system, also suitable membranes are being identified and developed for the on-site separation of hydrogen from a reaction mixture at 400 - 550 °C, 1-10 bar, and the typical steam reforming environment comprising  $H_2/CH_4/CO_2/CO$  and steam.

CoMETHy focuses on “composite membranes” in order to minimize the Pd layer thickness and, hence, limit materials costs. Particularly, the following hydrogen selective membrane types with a Pd-based layer deposited on a porous support are considered:

- Pd (alloy) supported on asymmetric porous stainless steel, with an inter-metallic ceramic layer and a limited Pd layer thickness ( $< 5 \mu m$ ).
- Pd (and Pd-Ag) on porous ceramic supports by electroless plating (EP).
- Pd (and Pd-Ag) on porous ceramic supports by “two-layers” deposition, obtained by combination of EP with physical vapour deposition.

For comparison, the performance of developed membranes is benchmarked with self-supported Pd-Ag membranes, consisting of a rolled Pd-Ag foil (thickness  $> 50 \mu m$ ).

In Fig. 5 is shown a tubular composite membrane developed. The picture also shows the black ring spacers placed on the membranes in order to hold the catalytic foam and physically separate it from the membrane. In Fig. 5 it is also shown a microscopic image of the selective Pd-based layer coated on the porous support.



Fig. 5. Example of supported Pd-based membrane developed in CoMETHy.

Some composite tubular membrane prototypes are currently being tested in lab-scale integrated membrane reactors.

All developed membranes are tested under the typical conditions of the membrane reactor. In Fig. 6 some preliminary results on hydrogen permeance are reported.

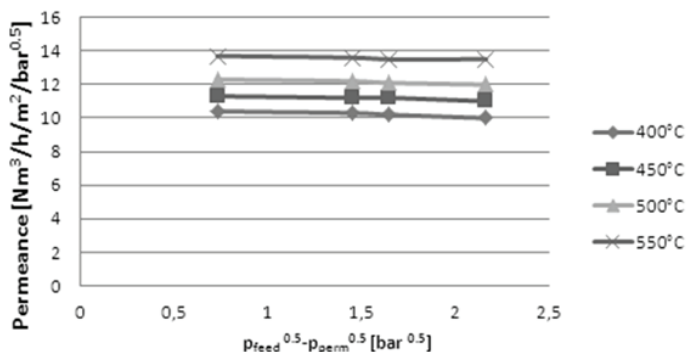


Fig. 6. Hydrogen permeance in preliminary tests on ceramic-supported Pd membranes.

### 5. Solar steam reformer design

After selection of the most suitable catalyst system and membrane, research has been focused on the integration of these components in a membrane reactor heated by molten salts. Two basic options have been considered:

1. Multi-stage (non-integrated) membrane reformer, where the membrane unit is separated from the catalytic bed, like in a multi-stage reactor-membrane train.
2. Integrated membrane reformer, where the membrane is integrated with the catalyst bed and the molten salts heat exchanger. An indicative sketch of the molten salts aided integrated membrane reformer is shown in Fig. 7.

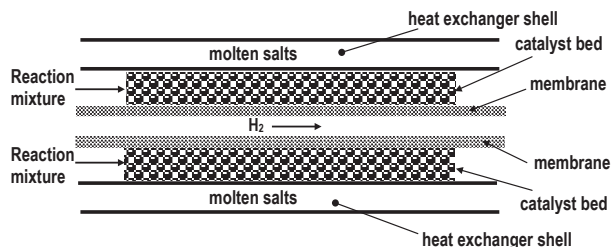


Fig. 7. Indicative sketch of molten salts powered membrane reactor.



In Fig. 8 are shown the drawings of an integrated membrane reactor with the molten salts flowing through the shell, and a three-stages non-integrated reactor [3].

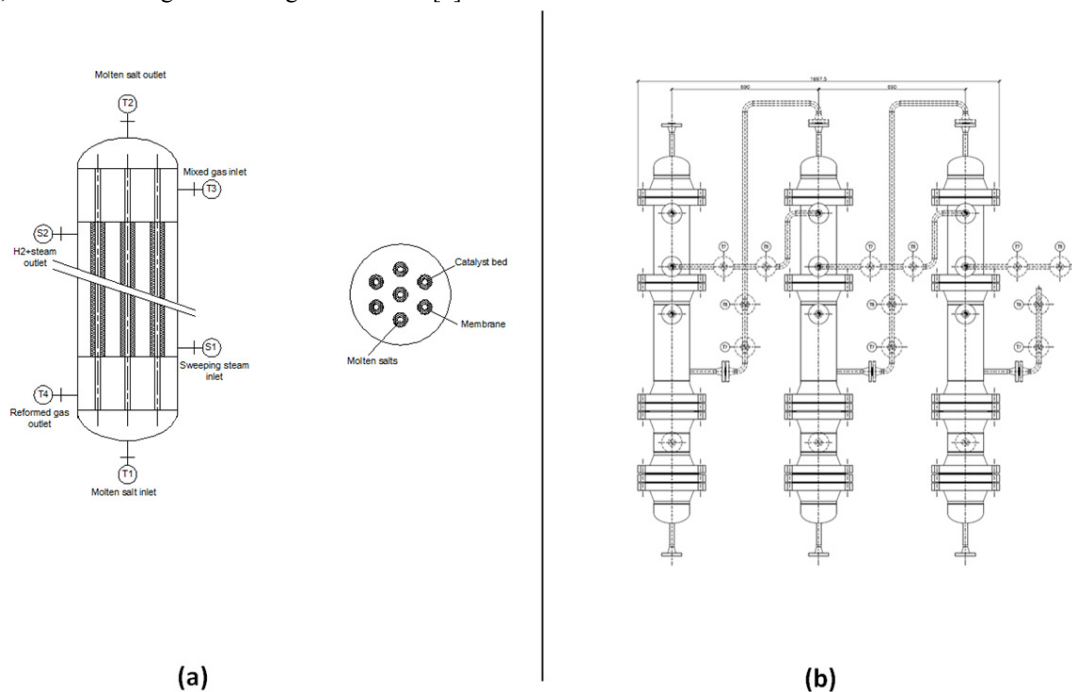


Fig. 8. Conceptual design drawings of the two solar reactor schemes developed in CoMETHy: integrated (a) and a three-stages non-integrated (b) membrane reformer (courtesy from Processi Innovativi Srl).

Both membrane reactor layouts (integrated and non-integrated) have pros and cons: besides technical considerations, the selection of the optimal configuration depends on the final application and optimization criteria. Pd-based membranes are compliant with the reactor temperatures (400-550°C), so an integrated system (Fig. 7, Fig. 8a) represents an attractive choice: it is more compact and allows single-pass higher efficiency. The development of this reactor is an engineering challenge involving design and mechanical issues, considering that the heat transfer rate should be not only synchronized with the reaction kinetics, but also with the membrane permeance. Results obtained in a test bench reactors have proved the feasibility of the integrated concept and performance profiles have been obtained. A pre-pilot (2 Nm<sup>3</sup>/h) prototype is now being built and installed in a molten salts loop for a final proof-of-concept.

## 6. Process integration with CSP

The obtained results are now being applied to make a process assessment and to identify the best strategies to couple the chemical process with the primary heat source, i.e. the CSP plant. Technical-economical assessment is also required to evaluate the competitiveness of the process for decentralized hydrogen production, identifying the best strategies to couple the CSP plant with the steam reforming plant.

It is clear that the extensive use of membranes and membrane reactors to drive the conversion will make the chemical plant more complex, but it also will make process more (energetically) efficient so the CSP plant size will be reduced. Therefore a compromise can be identified to foster industrial application of the technology for distributed and sustainable hydrogen production.



## 7. Summary and conclusions

An innovative solar reformer is being developed in the CoMETHy project. Besides the interesting potentials, its development involves different research topics: selection of advanced catalyst systems with enhanced heat transfer capability and selective composite membranes, and the identification of the best options for catalyst/membrane assembly, and reformer coupling with the CSP plants.

## Acknowledgements

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