Development of a Solar-Powered, Fuel-Flexible Compact Steam Reformer: The CoMETHy Project

Alberto Giaconia[a,*], Luca Turchetti[a,n], Giulia Monteleone[a], Barbara Morico[b],
Gaetano Iaquaniello[b], Keren Shabtai[c], Moshe Sheintuch[d], Daniella Boettge[e],
Joerg Adler[e], Vicenzo Palma[f], Spyros Voutetakis[g], Angela Lemonidou[h],
Maria Christina Annesini[i], Marcel den Exter[l], Harald Balzer[m]

[a]ENEA (Italy); [b]Processi Innovativi Srl. (Italy); [c]Acktar Ltd. (Israel); [d] Technion - Israel Institute of Technology (Israel); [e]Fraunhofer Institute for Ceramic Technologies and Systems (Germany); [f]University of Salerno (Italy); [g]Centre for Research and Technology Hellas, CPERI/CERTH (Greece); [h]Aristotle University of Thessaloniki (Greece); [i]University of Rome La Sapienza (Italy); [l]Energy Research Centre of the Netherlands, ECN (The Netherlands); [m]GKN Sinter Metals (Germany); [n]University Campus Biomedico of Rome (Italy).
alberto.giaconia@enea.it.

This paper presents 7FP 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.

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 renewables (solar and 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:

$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (3n+1)H_2 \tag{1}$$

where C_nH_{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

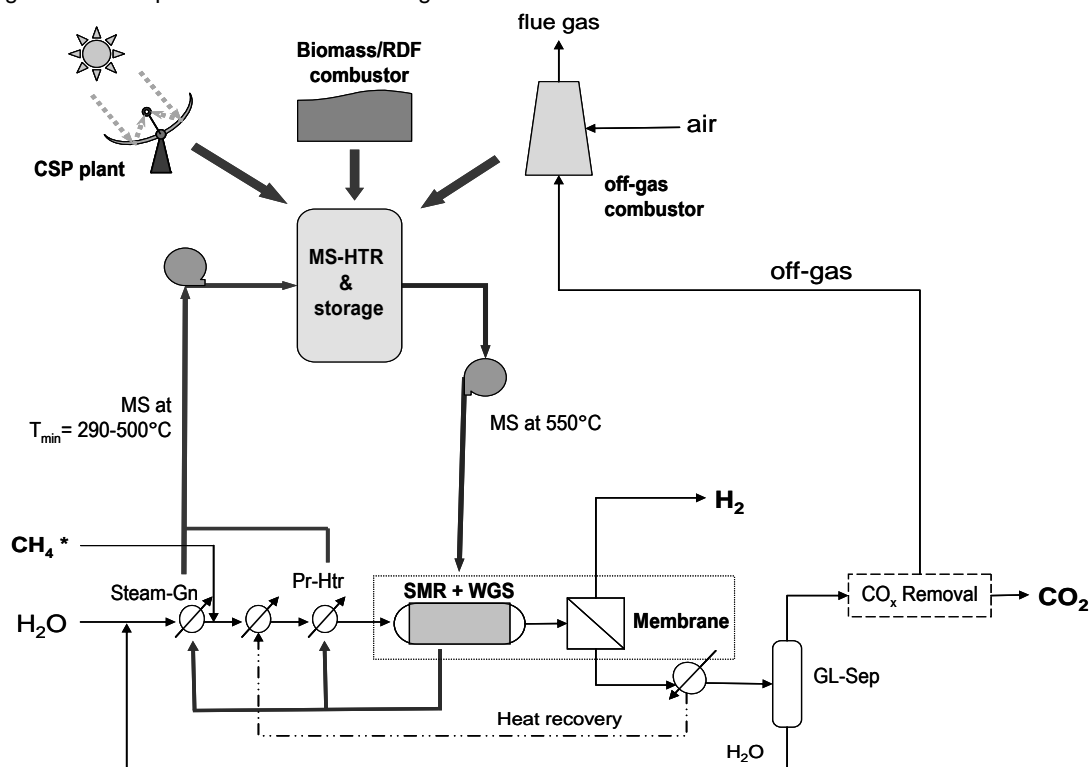A general concept scheme is shown in Figure 1.

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

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 $NaNO_3/KNO_3$ (60/40 w/w), often called "solar salts". This allows coupling with Concentrating Solar Power (CSP) plants using this molten salts mixture as thermal storage system at temperatures up to 550 °C. Accordingly, this fluid collects heat from the different available heat sources and transfers it to the thermochemical plant.

A suitable heat storage system 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, as reported by Giaconia et al. (2007) and by De Falco et al. (2009).

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 850-950 °C down to 400-550 °C, with consequent significant gain in material costs since no special steel alloy for high-temperature operation is 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 400-550 °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.

When the thermochemical plant is powered by solar heat, in principle, there will be no combustion in the whole process, and no CO_2-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, as reported by Giaconia et al. (2008). 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: Moeller et al. (2006) foresee a breakeven point for the hydrogen production cost, resulting in a solar route economically more convenient than the fossil based one. The same solar steam reforming process applied to biomass derived fuels (i.e. biofuels like biogas, bioethanol, etc.) allows totally renewable hydrogen production.
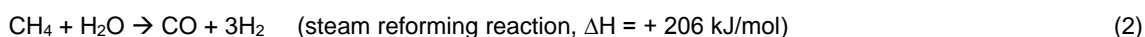
An additional advantage of the use of molten salts as heat transfer fluid for steam reforming is when some stand-by periods of the plant are foreseen, as it is the case of small-medium scale reformers for hydrogen refueling stations. In this case, the continuous molten salts recirculation eases the overall 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 feedstock have been chosen in the perspective of the multi-fuel application: methane-rich gas (e.g. natural gas), CH_4/CO_2 mixtures (up to 50 %vol. CO_2, 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. CoMETHy's R&D tasks

3.1 Catalytic materials for low-temperature steam reforming

Specific catalyst formulations are being proposed, developed and characterized for the steam reforming of the three reference feedstock: pure methane, CH_4/CO_2 (1:1) mixtures to simulate a biogas, and ethanol.

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

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \text{(steam reforming reaction, } \Delta H = + 206 \text{ kJ/mol)} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \text{(WGS reaction, } \Delta H = - 41 \text{ kJ/mol)} \tag{3}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \text{(dry reforming reaction, } \Delta H = + 246 \text{ kJ/mol)} \tag{4}$$

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 h-on-stream).

Preliminary results show that Ni- and Rh- based catalysts supported on CeO_2 or mixed Ce/Zr/La oxides exhibit high activity and stability towards CH_4 steam reforming even at low temperatures, also enhancing the WGS reaction (WGS equilibrium is almost attained). As an example, in Fig. 2 depicts the experimental points obtained over Ni/CeO_x catalyst with a "simulated" biogas ($CH_4:CO_2$ = 1:1 v/v) steam reforming at 400-550 °C and 1 atm, steam-to-carbon S/C = 3 ($H_2O:CH_4$ v/v) compared with the thermodynamic equilibrium curves, with relatively low outlet CO concentration (< 5 %vol. on dry basis).

Catalyst stability in the presence of typical gas contaminants, like H_2S in the ppm range and higher hydrocarbons in the 1-10 %vol. range, is evaluated too.

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

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad \text{(ESR, } \Delta H = + 144 \text{ kJ/mol)} \tag{5}$$

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_4 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$_2$) seem a good choice according to preliminary results.
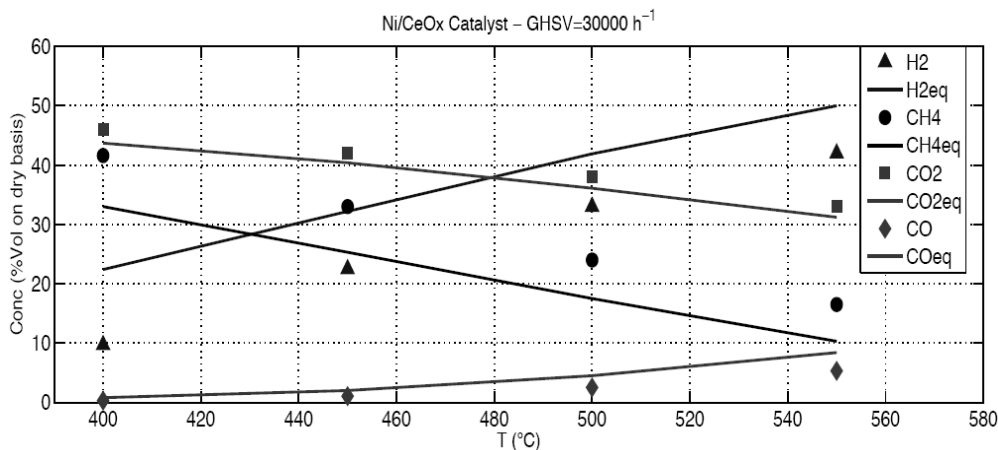

Figure 2: Comparison between outlet gas composition (dry basis) obtained in steam reforming of a "simulated" biogas (CH_4:CO_2 = 1:1 v/v) and thermodynamic equilibrium. Catalyst: Ni (10 %wt.)/CeO$_2$, 250 - 355 μm pellets. Operating conditions: 400 - 550°C, 1 atm, S/C = 3.0, Gas Hourly Space Velocity (GHSV) = 30,000 h^{-1}

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:

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 drops. 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 (Turchetti et al. 2011). 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 void fraction and porosity is investigated with a specific experimental campaign, aimed at the evaluation of the heat transfer properties and pressure drops. Three developed SiC samples with different porosity are shown in Figure 3. The options for the best fitting of the ceramic foams in the reactor are also studied.

The selected catalytic material will be coated on the selected ceramic structures and the overall catalytic system performance will be evaluated.

Figure 3: SiC-made ceramic open foam samples for catalyst support

3.3 Membrane development

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 μm).

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 μm).

All developed membranes are tested under the typical conditions of the membrane reactor. In Figure 4 some preliminary results on hydrogen permeation are reported.
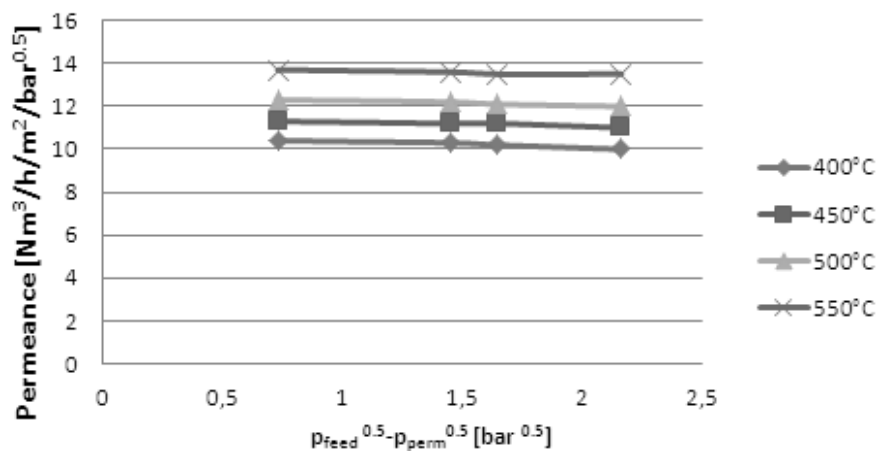

Figure 4: Hydrogen permeance in preliminary tests on ceramic-supported Pd membranes

At the end of this activity, most suitable membranes will be selected to be tested in the membrane reactors.

3.4 Solar steam reformer design

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

1. Multi-stage membrane reformer with the membrane external to the reactor.
2. Integrated system with the membrane integrated with the catalyst and the heat exchanger.
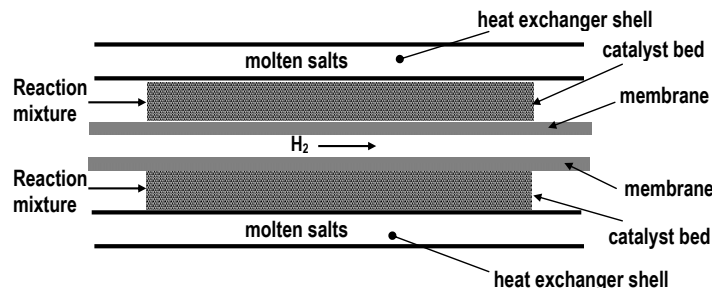

Figure 5. Indicative sketch of molten salts powered membrane reactor

Pd-based membranes are compliant with the reactor temperatures (400-550 °C), so an integrated system (Figure 5) is first the preferred 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. The developed reactor will be first studied at the laboratory scale level; after, a pre-pilot (2 Nm^3/h) prototype will be built and installed in a molten salts loop for proof-of-concept.

3.5 Process integration with CSP

The obtained results will be 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.

Membrane exploitation 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.

4. 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

References

Giaconia A., Grena R., Lanchi M., Liberatore R., Tarquini P.,2007, Hydrogen/methanol production by sulfur–iodine thermochemical cycle powered by combined solar/fossil energy, Int. J. Hydrogen Energ. 32, 469-481.

De Falco M., Giaconia A., Marrelli L., Tarquini P., Grena R., Caputo G., 2009, Enriched methane production using solar energy: an assessment of plant performance, Int. J. Hydrogen Energ 34 98-109.

Giaconia A., De Falco M., Caputo G., Grena R., Tarquini P., Marrelli L., 2008, Solar steam reforming of natural gas for hydrogen production using molten salt heat carriers, AIChE J. 54, 1932-1944.

Moeller S., Kaucic D., Sattler C., 2006, Hydrogen production by solar reforming of natural gas: a comparison study of two possible process configurations, ASME J, Sol. Energy Eng. 128, 16–23.

Turchetti L., Monteleone G., Annesini M.C., 2011, Comparative Analysis of Heat Transport in Sic Solid Foam and Al2o3 Granular Packings for Fixed-bed Reactors, Chem. Eng. Trans. 24, 1405-1410