

## **Scale Down of Reforming Processes for Hydrogen Production from Renewable Sources**

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Hydrogen has attracted much interest as energy carrier, both as feed for fuel cells or as an environmentally friendly fuel for automotive and a transition from a fossil fuel to a hydrogen-based economy has been forecasting for the 2050s. Nowadays, major issues concerning a wide use of hydrogen are related to the lack of a proper H<sub>2</sub> grid and problems related to hydrogen storage (mainly due to the low energy density and safety issues). Scale down of the production, allowing a decentralized hydrogen production (close to the end-user), or production on-board of vehicles can bypass these problems.

Traditionally, hydrogen is widely used in the chemical industry and it is mainly produced by natural gas (NG) reforming, an endothermic process that demands a large heat input and, due to the equilibrium limitations, high temperature to obtain large conversion. Furthermore, this process requires the integration of different units (the reformer itself, the water gas shift reactor and separation units to recover hydrogen)

The challenges for scale down are mainly related to the success in reducing the operating temperature, simplifying the reforming process with integrated units and using liquid feedstock. The use of renewable sources both as feedstock for the reforming and to supply the energy required for endothermic process is also advisable for process sustainability.

If reforming is carried out at moderate temperatures (400-500°C), a significant gain in material costs can be achieved; furthermore, at these temperatures, concentrating solar power equipment can be used as energy source for sustaining the hydrogen-producing endothermic reaction, thus reducing the carbon footprint of the process. On the other hand, thermodynamics limit the conversion at 30-40%. Therefore, two approaches have been considered.

The first one, carried out with the financial support of the METISOL project of the Italian Environment Ministry, is to exploit the possibility to produce an enriched methane mixture (EM) with a hydrogen content between 10 -30% v/v; such a mixture can be used as feedstock in the traditional natural gas IC engines to improve the engine efficiency and to reduce the emission of green house gases; furthermore EM can be stored and distributed by the standard NG storage systems or medium pressure grid [1]. Indeed if the process is aimed to EM production, hydrogen does not have to be separated from unreacted CH<sub>4</sub>, but separation units to remove carbon dioxide are required [2].

The second one is to use membrane reactors (MR), comprising a palladium or palladium-silver membrane, to overcome the thermodynamic limitation by separating hydrogen from the reacting mixture. Indeed, these membranes have an infinite selectivity for hydrogen and two goals can be achieved: a) the hydrogen separation shifts the reaction towards the product and allow to reach high conversion even at low temperature, b) hydrogen with a very high degree of purity, as required for fuel cells, is obtained. These considerations are at the basis of the CoMETHy (Compact Multifuel-Energy to Hydrogen converter) project co-founded by the European Union's Seventh Framework Programme (FP7): the project's aim is to develop a compact solar steam reformer to convert different reformable fuels to hydrogen [3, 4]. The basic idea is to carry out a low temperature steam reforming in a membrane reactor using solar energy in a molten salt concentration solar plant as main energy source; CSP plant hybridization, which can be achieved with combustion of biomass or refuse derived fuel (RDF) or off-gas, is considered as the best compromise between CSP and back-up fuel duties. The development of this technology involves a number of R&D challenges: it is necessary to identify suitable catalysts in the operational temperature range [5] and membrane; subsequently it has been necessary to integrate all the components in a membrane reactor heated by molten salts. Indeed, the presence of the costly membrane should be limited to the zone of the reactor where it is most effective, i.e. once a significant amount of hydrogen has been produced. In other words, a conventional pre-reformer reactor (without the membrane), followed by a membrane reactor are included in the process scheme. In this way, the membrane

reactor is fed with a reforming gas at the equilibrium condition and almost constant temperature can be considered in this reactor.

A detailed analysis of the behavior of membrane catalytic reactor has been carried out, by means of a two-dimensional axial symmetric isothermal model, in which all of the mass transport mechanisms are taken into account together with their coupling to momentum transport [6-7]. The analysis of the species profile within the membrane reactor unveils the existence of different transport-reaction-permeation regimes, each characterized by qualitatively different concentration profiles along the radial and axial coordinate. Different limiting-case scenarios can be also considered [8]: in the first one the reaction is slow compared to hydrogen transport and the reactor behaves as a separator; in the second one the reaction is infinitely fast – as usually occurs with the available catalysts – and the hydrogen is produced as soon as it is removed by permeation, so that the system is everywhere in equilibrium. In both cases, the hydrogen permeation may be limited by either transport across the membrane or transport within the catalytic bed. In all these cases, simple models can be used to evaluate integral quantities, such as hydrogen permeate flow rate and yield [9-11]. The reactor performance is measured by the bare-separator efficiency (the ratio of the hydrogen permeate to the hydrogen flow rate entering the membrane reactor): this parameter, larger than unity as a result of the significant advancement of the reaction due to the hydrogen permeation through the membrane, shows a maximum in correspondence to a critical pressure.

Common to all of these regimes, the existence of a reaction boundary layer near the membrane is uncovered, which defines the fraction of the total catalyst volume that is actually useful for the reaction progress. This observation raises an obvious question as to what operating conditions and reactor geometry should be used in order to minimize the extent of the inactive catalyst volume fraction. It was found that optimal efficiency can be obtained by tuning the thickness of the catalyst bed to that of the boundary layer [12].

Different hydrogen containing feedstock can be also considered as reformable fuel for decentralized hydrogen production: in particular, liquid reformable feedstock, like methanol or ethanol, can offer the advantage of high volumetric energy density, while fuel from renewable sources, like biogas (CH<sub>4</sub>/CO<sub>2</sub> mixture with up to 50% of carbon dioxide) or bioethanol, could bring significant environmental benefits, mainly in terms of reduction of the carbon footprint of the whole process [3-4]. Hydrogen production by steam reforming of ethanol encounters also the problem that the reforming reaction is accompanied by the formation of various by-products, which affect the selective production of hydrogen. In this case, hydrogen separation in a membrane reactor not only shifts the equilibrium conversion, but also shifts the product distribution in the desired direction. This effect has been demonstrated in a Pd membrane reactor packed with a Pt/Ni-CeO catalyst, obtaining very high hydrogen yield (about 4.5 mol H<sub>2</sub>/mol ethanol at 500°C) with low steam-to-ethanol ratio and moderate pressure level [13].

Process intensification to favor decentralized hydrogen production can also be carried out coupling endothermic and exothermic reactions, e.g. coupling methane steam reforming with a combustion in autothermal reforming (ATR); in this way it is possible to reduce the fuel consumption and to work with smaller plants. Traditionally, ATR is carried out in reactors formed by a combustion chamber and a catalytic section; in this configuration all the heat is released immediately after the inlet section and a temperature peak is observed, with problems in terms of reactor control and resistance of catalyst and construction materials. Two alternative configurations have been considered [14]: in the first one the two reactions (the exothermic catalytic combustion providing the heat to drive the endothermic steam reforming) are carried out in two spatially separated chambers, with a thin wall between the two chambers which is the only resistance to heat transfer; in the second one, only part of the oxygen is mixed with the SR feed, whereas the remaining portion is distributed along the reaction axis. In both case smooth thermal profiles are obtained. Coupling of endothermic and exothermic reactions in a membrane reactor is also considered for oxidative steam reforming of ethanol: in this case, a self-supported Pd-Ag membrane is used in a catalytic reactor filled with a commercial Pd catalyst, fed with a diluted water-ethanol mixture and air; a hydrogen yield of 4.1 is obtained at 450°C and 200 kPa [15].

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