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# Multi-tube Pd–Ag membrane reactor for pure hydrogen production

Silvano Tosti\*, Fabio Borgognoni, Alessia Santucci

ENEA, Unità Tecnica Fusione, C.R. ENEA Frascati, Via E. Fermi 45, Frascati (RM) I-00044, Italy

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## ABSTRACT

An experimental apparatus carrying out a membrane process for producing pure hydrogen via ethanol steam reforming has been tested in order to measure the hydrogen production by varying operative parameters such as temperature, pressure and membrane sweeping mode. The process consists of a traditional fixed bed reformer, which performs the ethanol steam reforming, and a multi-tube Pd–Ag membrane reactor, where both the water gas shift reaction and the separation of pure hydrogen take place. The water gas shift membrane reactor uses permeator tubes of wall thickness 50–60  $\mu\text{m}$ , diameter 10 mm and length 250 mm.

The experiments have been carried out with a reaction pressure in the range 100–250 kPa, while the reformer has been operated at a temperature of 690–890  $^{\circ}\text{C}$  with feed water/ethanol molar ratio of 10.5/1 and flow rates between 200 and 500  $\text{g h}^{-1}$ . The hydrogen has been recovered in the shell side of the membrane module by vacuum pumping or inert gas (nitrogen) sweeping at 350–400  $^{\circ}\text{C}$ . The highest hydrogen productions (about 3.5  $\text{NL min}^{-1}$ ) have been attained by feeding 500  $\text{g h}^{-1}$  of water/ethanol mixture and by recovering the hydrogen through vacuum pumping in the shell side of the membrane module at 400  $^{\circ}\text{C}$ .

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## 1. Introduction

The decreasing availability of fossil fuel reserves and the increasing level of green-house gases in the atmosphere are re-orientating the researchers' activities towards alternative energy sources [1,2]. The biomasses can substitute the traditional fossil fuels, but their use would not reduce significantly the environmental pollution. In fact, the biomasses production from dedicated bio-energy crops (i.e., corn, potatoes, sugar cane, etc.) is quite energy demanding because of its large use of nitrogen-based fertilizers and water: furthermore, the production of this kind of biomasses has recently been responsible for the increase in the price of food [3]. In this view, a second generation of bio-fuels produced from less expensive materials such as lignocellulosic wastes coming

from agricultural and wood industries can be considered as  $\text{CO}_2$  neutral and not affecting the food production [4,5].

Presently, the transport sector covers about 60% of the global energy demand, and the introduction of bio-fuels (bio-ethanol and bio-diesel) into traditional internal combustion engines is expected to be increasing. However, a medium-long term strategy aimed at increasing the energy efficiency and, in the meanwhile, at decreasing the local emissions of the transportations, should consider the use of cars with PEM fuel cells fed by hydrogen [4,6]. For these reasons, the attention of several research groups has focused on the production of hydrogen from bio-ethanol [7–9].

Based on these considerations, a work aimed at producing hydrogen from ethanol steam reforming has been carried out [10–12]. Pure hydrogen should be used to feed a PEM fuel cell

\* Corresponding author.

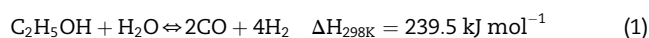
E-mail address: [silvano.tosti@enea.it](mailto:silvano.tosti@enea.it) (S. Tosti).

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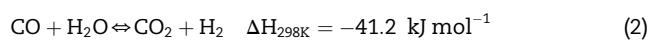
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on electrical vehicles, where an ethanol fuel tank is located: in this way, hydrogen storage, transportation and safety problems could be avoided. In order to be hosted on-board, the ethanol reformer has to be characterized by high efficiency and, possibly, reduced size: for these reasons, a membrane process using Pd–Ag permeators has been developed. Among the separation processes, the membrane technologies present many advantages such as continuous operation, modularity and energy saving. Particularly, membrane reactors are devices where a catalyzed reaction and a separation take place simultaneously. When a dehydrogenation reaction is carried out in a membrane reactor where the membrane is selectively permeable to hydrogen, the continuous removal of one of the reaction products (the hydrogen) permits to promote the reaction conversion (shift effect) also beyond the thermodynamic equilibrium [13–15]. For separating and producing hydrogen, several configurations (disks, tubes, etc.) and different kinds of Pd-based membranes have been studied: their hydrogen selectivity and permeability mainly depends on the nature of the metal layer (dense membrane or thin metal films coated on porous supports) [16,17]. Pd–Ag thin wall tubes produced by cold-rolling and diffusion welding are characterized by a reduced use of the precious metal alloy (tube wall thickness of 50–60  $\mu\text{m}$ ) and consequently reduced cost, infinite hydrogen selectivity and good durability [18,19]. As a consequence of their high permeability and complete selectivity, when applied to membrane reactors, these membranes allow both the production of ultra-pure hydrogen and the maximization of the shift effect.

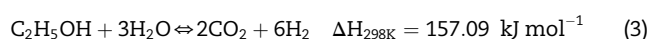
The ethanol steam reforming is an endothermic reaction which produces carbon oxide and hydrogen:



Subsequently, the water gas shift reaction (WGS) permits to convert CO into  $\text{CO}_2$ , thus producing further hydrogen:



Considering the complete process, the reaction is:



In order to produce hydrogen from ethanol reforming via membranes, a two-step process consisting of a traditional reformer operating at high temperature (700–800  $^\circ\text{C}$ ) performing the reaction (1) followed by a Pd–Ag multi-tube module has been studied [12]. In the membrane module, the water gas shift reaction (2) and the hydrogen separation take place simultaneously at 350–400  $^\circ\text{C}$ . The WGS is an exothermic reaction strongly affected by temperature: as a matter of fact, in the reformer which operates at high temperature the thermodynamic equilibrium of reaction (2) is practically shifted towards the reverse WGS reaction (conversion of  $\text{CO}_2$  into CO).

The catalyst materials used in traditional reactors operating at high temperature (600–800  $^\circ\text{C}$ ) for the ethanol steam reforming are based on Rh, Ru, Pd, Pt, Ni, Co and Cu [20–29]. In particular, the design of the two-step process has considered for the ethanol reformer the use of an Rh-based catalyst supported on alumina [30]. Under the design operating conditions described in the previous work [12], about 5.5 mol

of hydrogen per mole of ethanol fed are expected to be produced in the traditional reformer, while in the membrane module about 0.5 mol of hydrogen comes from the conversion of CO into  $\text{CO}_2$  through the water gas shift reaction.

For the water gas shift reaction two kinds of catalysts are proposed, for low (190–210  $^\circ\text{C}$ ) and high temperatures (350  $^\circ\text{C}$ ), respectively. Among the materials studied for promoting the WGS the Pd is reported as active metal [31] and recent works describe the use of Pd supported over ceria [32–34]. Particularly, at high temperature the capability of the Pd–Ag membranes of catalyzing the WGS is unaffected by the support [32].

This paper describes the tests carried out with an experimental apparatus which has been operated according to the scheme of the two-step process. The hydrogen production under different operating conditions (temperature, pressure, sweep mode) has been investigated as well as the results obtained with and without WGS catalyst inside the membrane reactor have been compared.

## 2. Experimental setup

The testing apparatus is shown in the scheme of Fig. 1. Its main components are:

- a pressurized water/ethanol mixture container,
- a fixed bed traditional reformer,
- a condenser,
- a multi-tube Pd–Ag membrane module.

The membrane module is a membrane reactor where a finger-like configuration of the Pd–Ag tubes inside the shell module is adopted, see Fig. 2. In such a mechanical configuration described in a previous work [12], one end of the permeators is closed and the feed stream coming from the reformer is introduced into the membrane lumen through a stainless steel tube. The feed stream which consists of water, CO, hydrogen and unreacted reagents of the reforming unit passes along all the catalyst bed while the hydrogen produced by the reaction (2) and coming from the reformer permeates the Pd–Ag membrane and is recovered in the shell side. Since the Pd–Ag tubes are fixed to the module at only one end, the free elongation/contraction consequent to the thermal and hydrogenation cycles is permitted and a good durability is ensured [19].

The water–ethanol mixture coming from a container pressurized by a nitrogen bottle is fed inside the ethanol steam reformer through a liquid mass flow controller (L MFC). During the catalyst regeneration or the permeation tests, hydrogen can be sent into the reformer via a gas mass flow controller (G MFC). By leaving the reformer, the gas stream enters a condenser (air cooled) where the largest part of the liquid phase is collected. Finally, in the lumen side of the Pd–Ag tubes, the water gas shift reaction and the hydrogen separation take place. Hydrogen, which permeates the membrane tubes, is collected in the shell side of the membrane module by sweeping with an inert gas (nitrogen) or by vacuum pumping. The inert gas stream is sent into the shell side through a gas mass flow controller (G MFC) while the

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