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Palladium based membranes and membrane reactors for hydrogen production and purification: An overview of research activities at Tecnalia and TU/e

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ABSTRACT

In this paper, the main achievements of several European research projects on Pd based membranes and Pd membrane reactors for hydrogen production are reported. Pd-based membranes have received an increasing interest for separation and purification of hydrogen. In addition, the integration of such membranes in membrane reactors has been widely studied for enhancing the efficiency of several dehydrogenation reactions. The integration of reaction and separation in one multifunctional reactor allows obtaining higher conversion degrees, smaller reactor volumes and higher efficiencies compared with conventional systems. In the last decade, much thinner dense Pd-based membranes have been produced that can be used in membrane reactors. However, the thinner the membranes the higher the flux and the higher the effect of concentration polarization in packed bed membrane reactors. A reactor concept that can circumvent (or at least strongly reduce) concentration polarization is the fluidized bed membrane reactor configuration, which improves the heat transfer as well. Tecnalia and TU/e are involved in several European projects that are related to development of fluidized bed membrane reactors for hydrogen production using thin Pd-based (<5 μm) supported membranes for different application: In **DEMCAMER** project a water gas shift (WGS) membrane reactor was developed for high purity hydrogen production. **ReforCELL** aims at developing a high efficient heat and power micro-cogeneration system (m-CHP) using a methane reforming fluidized membrane reactor. The main objective of **FERRET** is the development of a flexible natural gas membrane reformer directly linked to the fuel processor of the micro-CHP system. **FluidCELL** aims the Proof-of-Concept of a m-CHP system for decentralized off-grid using a bioethanol

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reforming membrane reactor. **BIONICO** aims at applying membrane reactors for biogas conversion to hydrogen. The fluidized bed system allows operating at a virtually uniform temperature which is beneficial in terms of both membrane stability and durability and for the reaction selectivity and yield.

Introduction

On an industrial scale, hydrogen is currently mainly produced by reforming of natural gas, an endothermic reaction system carried out at high temperature (>850 °C) followed by high and low temperature water-gas-shift reactors and final hydrogen purification step(s) (see Fig. 1) [1]. This conventional system is only efficient at very large scales, where heat integration can be optimized and the excess heat can be exported in the form of steam/power. The main problems for the reaction system are the thermodynamic constrains that limit both the steam methane reforming (endothermic) and water gas shift reactions (exothermic). To achieve high conversions and high hydrogen yields with high efficiencies, complex heat integration is required [2]. Until today, this process is still responsible of considerable greenhouse gas emissions since carbon dioxide capture actions are not implemented at industrial scale. Furthermore, the system cannot be easily scaled down and becomes rather inefficient at smaller scales. The efficiency of the process can be increased by exploiting process integration and process intensification. In this respect, integrating hydrogen production reactions and hydrogen recovery through membranes (named membrane reactors) results in shifting of the equilibria and thus higher efficiencies can be obtained. In **ReforCELL** project the steam and autothermal reforming (SMR/ATR) of methane was studied using membrane reactors. In **FERRET** the same reactions are being studied but using flexible natural gas as feed. In **DEMCAMER** project, a water gas shift (WGS) membrane reactor using Pd membranes was studied as an intensified process. When looking to remote installations, far away from natural gas grids and/or electrical grids, hydrogen can be produced from bio-renewable feedstocks. Among the various feedstocks, bioethanol is one of the preferred renewable sources for hydrogen production thanks to its unique features. Its hydrogen capacity is relatively high; it is easier to handle than hydrogen gas, being liquid and non-toxic; and even better, it is produced at global scale [3]. The bioethanol reforming using membrane reactors is being studied in **FluidCELL** project. Biogas is another renewable source for hydrogen production and it is produced during anaerobic digestion of organic substrates, such as manure, sewage sludge, the organic fractions of household and industry waste, and energy crops. It is produced in large scale digesters found preliminary in industrial countries, as well as in small scale digesters found worldwide. Biogas is also produced during anaerobic degradation in landfills and is then referred to as landfill gas. The European Biomass Organisation (AEBIOM) estimated a production of 39.5 Mtoe (≈48 bcm) in 2020, which corresponds to approximately 10% of EU natural gas consumption [4]. It must be outlined that the biogas production in the European Union has steadily increased over the last years. The biogas reforming membrane reactor is being evaluated in **BIONICO** project.

Pd-based membranes are mostly used for ultra-high H_2 purification due to their high H_2 permeances and selectivities compared to other materials. These membranes may be classified into unsupported and supported ones. Unsupported membranes are generally thick self-standing films (>50 μm thick) in order to have a minimum mechanical stability. The main drawback of these membranes is their low hydrogen permeance associated to their bulk diffusion resistance. Moreover, as palladium is very expensive and since the permeation flux decreases with increasing the membrane thickness (i.e. more membrane area is required for the same hydrogen flow for thicker membranes) the costs of the membrane separation sharply increase by increasing the

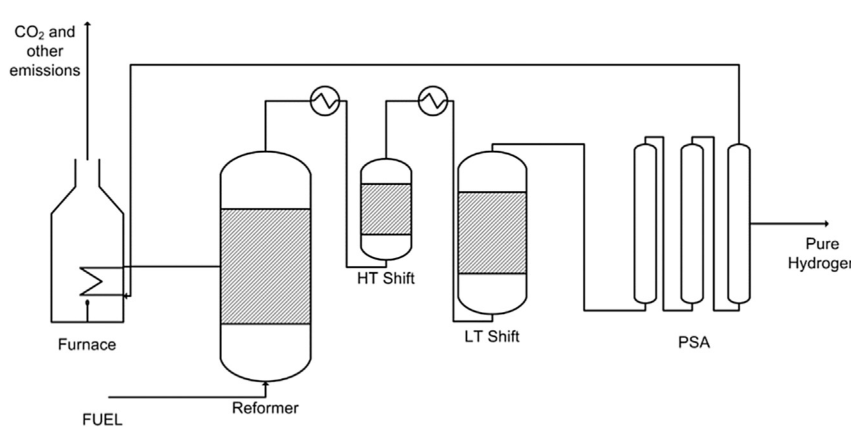

Fig. 1 – Conventional steam reforming reaction scheme. HT shift and LT shift are high and low temperature shift reactors respectively [1].