

# USING Pd/Ag MEMBRANES AND CATALYTIC WATER GAS SHIFT IN A PLUG FLOW REACTOR TO OBTAIN ULTRAPURE HYDROGEN AND TO INCREASE HYDROGEN YIELDS FROM SYNGAS

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In this work, we tested two technologies to improve hydrogen yield and quality from a stream of syngas. Stream of ultrapure hydrogen and high yields can be obtained by using membrane reactors (MR) which are based on the selective permeation of hydrogen through Pd membranes. On the other side, the production of H<sub>2</sub> from a syngas can be increased through the reaction between CO and H<sub>2</sub>O in the WGS reaction. The equilibrium is favourable to H<sub>2</sub> formation at low temperature and high H<sub>2</sub>O /CO ratio, and the presence of a catalyst is required to achieve a sufficient fast kinetics for practical applications.

Hydrogen separation in reactive and unreactive devices was experimentally investigated at bench scale by using Pd-Ag permeation units and MRs connected in a train able to treat 0.25 Nm<sup>3</sup>/h (STP) of syngas. Mixes of H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, and eventually N<sub>2</sub>, were used to simulate the typical composition of the syngas obtained in a biomass gasification. The experiments were carried out using two parallel lines each made of one permeator and one MR. About 50 g of a commercial catalyst based on platinum and zirconium oxide is loaded in each MR. A design of experiments (DOE) was elaborated consisting of 6 test carried out at 4, 6 or 8 bar; 300 °C, 325 °C, 350 °C and steam flow 1.1, 1.5 and 2 times the stoichiometric value. The retentate and the permeate compositions and mass flow rate were analysed at different process conditions.

As results, first we measured a flow of H<sub>2</sub> permeated from a MR (filled with the WGS catalyst) that was on average 3.4 times higher than that measured with the (empty) permeator unit. The pre-permeation step increases the total flow of ultrapure H<sub>2</sub> but does not affect significantly the production of new H<sub>2</sub> from WGS and should be used only for the syngas in which the H<sub>2</sub> content is high. As regard the WGS, the highest conversion was obtained at the highest value of H<sub>2</sub>O/CO ratio, as thermodynamically expected. The pressure also acted positively on the yield because with the increasing of the pressure the H<sub>2</sub> permeation also increased and the removal of H<sub>2</sub> from the reaction side and shifted the reaction towards further H<sub>2</sub> formation. The temperature affected the process in two opposite ways: low temperatures favoured higher yields, whereas low temperature depressed H<sub>2</sub> permeation.

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