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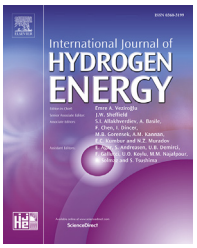

High pressure membrane separator for hydrogen purification of gas from hydrothermal treatment of biomass

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ABSTRACT

For hydrogen purification and green hydrogen production in the context of biomass hydrothermal gasification, a palladium membrane system with microchannels on feed and permeate side was studied. The high pressure in the product gas of the hydrothermal process could potentially be used to generate pressurized pure hydrogen on the permeate side. Stabilizing the membrane by an additional porous metal support, experimental verification of the concept was done at feed pressure up to 50 bar and permeate pressure up to 20 bar. The temperatures were varied between 370 °C and 425 °C. The device was found to be highly selective and efficient for pure hydrogen separation. The membrane was characterized regarding the hydrogen flux and a deviation of the permeation from Sievert's law above 30 bars feed pressure was found. Generally, the microchannels on the feed side minimized concentration polarization effects, leading to high hydrogen fluxes with hydrogen feed mixtures and with real gas samples from hydrothermal gasification.

Introduction

For energy supply, biomass as a renewable feedstock is an option amongst others. Different types of biomass usage are discussed, such as generating substitute natural gas, liquid fuels or chemicals from the organic feedstock – either in direct routes or via gasification. One option in gasification of the feedstock is the hydrothermal treatment of wet biomass. It could be used to generate an energy rich gas, either with focus on small hydrocarbon molecules/methane or on a hydrogen rich gas stream [1]. No drying of the biomass is required here. The hydrogen produced by hydrothermal gasification will in all cases contain certain amounts of carbon species such as methane, CO and CO_2. The latter can be removed in a washing step [2,3]. If hydrogen should be used in a low temperature fuel cell, e.g. PEM-type, the purification from methane and other carbon species is a necessary step to meet the fueling requirements, i.e. to avoid fuel cell degradation [4]. Though, an efficient separation process or device is demanded. A membrane separator based on palladium or its alloys as well as pressure swing adsorption could potentially fulfill the purity requirements. Generally, the application of palladium membranes in energy production recently got more

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and more attention [5,6]. Due to the high pressure of the product from the hydrothermal treatment with supercritical water a membrane system could theoretically – in contrast to pressure swing adsorption - be used to generate hydrogen under residual pressure, so that recompressing to 300–700 bar hydrogen pressure is much less costly. If hydrothermal gasification is conducted at > 250 bar and hydrogen content is > 50 vol% more than 125 bar hydrogen pressure are available at feed side, which means that at 20 bar hydrogen pressure on the permeate side more 84% of the hydrogen could be removed. This is of course only valid if the selectivity of the membrane is sufficient.

At KIT the demonstration plant VERENA (throughput up to 100 kg/h biomass) is available which actually produces hydrogen rich gas via supercritical water gasification at temperatures of 650 °C and pressures of 28 MPa [3,7]. Gas from this plant was filled in gas bottles and used for the studies presented here.

The device developed for separating the hydrogen from the VERENA gas at high pressure is based on a pure palladium membrane supported on a thin sheet of porous metal. The transport of hydrogen through a palladium foil is mostly described as a multi-step mechanism, i.e. adsorption, dissociation of hydrogen, diffusion in the palladium lattice, recombination and desorption. Diffusion inside the membrane is mostly considered as the rate limiting step (RDS) except for ultra-thin membranes where the actual transport distance is very low. In the case of diffusion inside the membrane as RDS, the permeability can then be described according to Fick's law and Sievert's law with the difference of the partial hydrogen pressure to the power of 0.5 on between feed/retentate and permeate side.

$$j_{H2} = \frac{Q}{s}\left(p_{H2,ret}^{0.5} - p_{H2,perm}^{0.5}\right) \quad (1)$$

Q represents the membrane permeability and s the thickness of the membrane. For the separation of hydrogen further aspects and phenomena across the membrane should be considered [8]: The removal of hydrogen in a gas flow parallel to the membrane surface may result in a considerable decrease of the partial pressure and therefore the driving force, i.e. no constant surface specific hydrogen flux through the membrane nor linear decrease of hydrogen concentration on feed side. Other gases can influence the separation result as they could block available sites for hydrogen adsorption and dissociation due to competitive adsorption. Finally, concentration polarization can reduce the hydrogen flux through the membrane; concentration polarization on feed side means that the hydrogen concentration towards the membrane surface may decrease due to a mass transport limitation in the laminar boundary layer above the membrane surface while hydrogen is removed too fast via the membrane. This effect may also occur and reduce the hydrogen flux through the membrane due to a stabilizing porous support on the retentate side; however, a sweep gas to reduce the partial pressure on the retentate side is a prerequisite that a concentration gradient towards the membrane may occur [9,10]. All these effects make it necessary to also have a closer look at the membrane device and the operation conditions itself. Microchannels promise to make concentration effects negligible due to a very low mass transport distance towards the membrane. Mejdell et al. used a microchannel configuration and could enhance the hydrogen flux through the membrane by avoiding concentration polarization [11]. In our manuscript, a microchannel membrane module with a porous support for the stabilization of the pure palladium membrane under high pressure is investigated. Concentration polarization may occur much easier at high pressure and high driving force. Hydrogen flux and hydrogen purity are essential parameters for the yield of hydrogen separation and the described concept of separating hydrogen at higher permeate pressure.

Material and methods

Setup

For the tests the following setup was used. With the setup hydrogen as well as mixtures of hydrogen and nitrogen could be dosed at pressures up to 50 bars on the retentate side and it was possible to build up 20 bars of pressure for the permeate side (see Fig. 1).

The test rig was equipped with three mass flow controllers (Brooks Series 5850), one of them for sweeping the permeate side channels. The pressure on the retentate side was controlled before and after the device. The backpressure was used as a reference for regulation by an automated needle valve. On the permeate side a manual back pressure regulator was used together with a pressure indicator.

The trans-membrane flow was determined by a soap film flow meter and two mass flow meters (Brooks Series 5850) were added especially for higher gas fluxes. For a constant outlet temperature, the flow was cooled with water in a heat exchanger. Additionally, the permeate flow as well as the retentate flow could be analyzed by an Agilent 7840s GC, equipped with a HP-Plot Q (30 m × 0.530 mm x 40.00 μm and HP-Molesieve columns (5 m × 0.530 mm × 25.00 μm).

The tested device itself was heated electrically from the outside with electric heating wire and for improved insulation packed in a box with an insulation powder (Freeflow®). The temperature control was done by a thermocouple on the surface of the pressure shell of the device. For better measurement two further thermocouples were inserted near permeate and retentate side into holes drilled in the pressure shell of the device (TI1 and TI2). In addition, a thermocouple was inserted in the preheated gas flow at the permeate inlet (TI3).

Membrane device

The device itself consists of two microstructured channel sheets facing each other. The channels have a length of 70 mm and a width of 0.12 mm. On each sheet 340 channels were fabricated. In between the palladium membrane with a thickness of 16 μm is located. For improved stabilization of the membrane a porous sinter metal sheet with pores of around 30 μm, a porosity of around 40% and 1 mm thickness (ITM - Plansee) is placed on the permeate side between the membrane and the channels because of the high pressure gradient.

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