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Procedia Engineering 44 (2012) 1117 – 1118

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[P1.176]

Hydrogen separation from multicomponent gas mixtures containing CO, N2 and CO2 using matrimid asymmetric hollow fiber membranes

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The application of hollow fiber membranes to industrial gas mixtures separation relies on the correct characterization of the permeation of the involved gaseous components through the hollow fiber membranes. Thus, this study is focused on the characterization of the permeation through Matrimid hollow fiber membranes of four H_2-containg binary gas mixtures (H_2/N_2, H_2/CO, H_2/CO_2) and the quaternary gas $H_2/N_2/CO/CO_2$ working at constant temperature of 303 K and pressures up to 10 bar. The main differences and similarities in the gas permeation properties of hollow fibers with respect to flat membranes as well as in the permeation of gas mixtures with respect to pure gases have been analyzed.

The fabrication of Matrimid hollow fibers was based on a dry wet spinning process, using the commercial polymer Matrimid 9715. Hollow fiber membrane modules were built by insertion of 1 fiber of ~10 cm length within a tubular stainless steel container in a counter-flow configuration. The hollow fiber modules were pressurized with the feed gas mixture at the bore side and an argon sweep gas was passed through the fiber shell to remove and transport the permeate stream to a gas chromatograph.

The pure and mixed gas permeation behavior of a Matrimid asymmetric hollow fiber membrane has been investigated over a broad range of concentrations for the separation of H_2 from N_2, CO and CO_2. Distinct gas separation performances were found for asymmetric hollow fibers in relation to thick flat dense Matrimid films. In the case of pure gas permeation, a higher membrane substructure resistance for CO_2 than for H_2 followed by N_2 and CO determines higher H_2/CO_2 and lower H_2/N_2 and H_2/CO ideal separation factors compared to flat membranes. At 2.3 bar feed pressure, ideal selectivity values obtained for H_2/N_2, H_2/CO and H_2/CO_2 gas pairs were of 74.4, 42.6 and 5 respectively. As in flat dense membranes, the permeance of H_2, N_2 and CO remained almost constant with pressure (up to 10 bar) with average values of 49.5 x 10^{-8} m^3 (STP) m^{-2} s^{-1} kPa^{-1} for H_2, 0.7 x 10^{-8} m^3 (STP) m^{-2} s^{-1} kPa^{-1} for N_2 and 1.2 x 10^{-8} m^3 (STP) m^{-2} s^{-1} $kPa^{-1}$for CO. In contrast, the permeance of CO_2 strongly increased with pressure, with values of 10.1 x 10^{-8} m^3 (STP) m^{-2} s^{-1} kPa^{-1} at 2 bar and 14.4 x 10^{-8} m^3 (STP) m^{-2} s^{-1} kPa^{-1} at 10 bar. This behavior is related to CO_2 induced accelerated plasticization in the asymmetric hollow fiber membrane due to a much thinner dense skin layer compared to the usual thickness of a flat dense membrane (0.1 ~ 0.5 □m compared to 30 □m).

In the case of the permeation of gas mixtures, as in flat membranes, competitive sorption effects determine a decrease in the permeation of H_2 with respect to pure gases, as shown in Fig. 1. For H_2/CO_2 binary mixtures this depression is higher than for H_2/N_2 or H_2/CO mixtures where it is almost null. Due to plasticization induced higher transport rates of H_2 in H_2/CO_2 mixtures, the decay in the permeation of H_2 is not as high as in flat membranes.

Our results suggest that for H_2 mixtures that contain CO_2 the hollow fiber membrane performance is better than that of flat membranes, and therefore using thick film data to design

doi:10.1016/j.proeng.2012.08.696

or select membrane materials only gives a rough approximation of the performance that might be reached in practice.

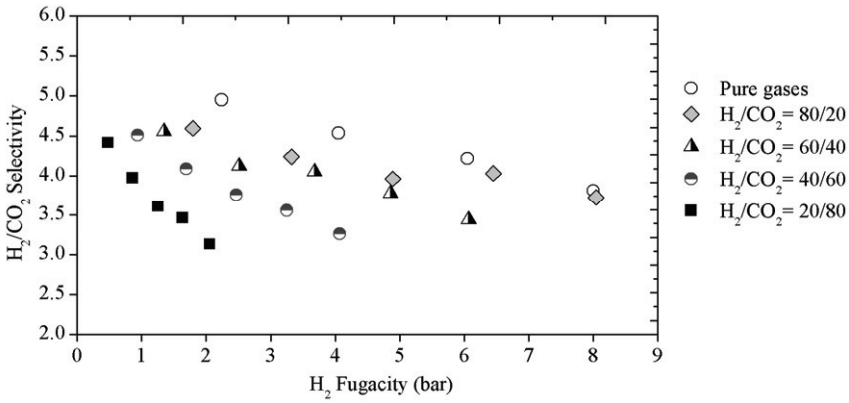

Fig. 1. H_2/CO_2 selectivity variation with the fugacity of H_2 for binary H_2/CO_2 mixtures in asymmetric Matrimid hollow fiber membranes.

Acknowledgments: Financial support from the Spanish Ministry of Science under the projects: ENE 2010-15585 and CTQ 2008-00690/PPQ is gratefully acknowledged.

Keywords: Hydrogen, Hollow fiber, Mixed gas separation, Polyimide membrane