

DEVELOPMENT OF CARBON MOLECULAR SIEVE MEMBRANES FOR THE USE OF RENEWABLE GASES, BIOMETHANE AND HYDROGEN IN NATURAL GAS NETWORKS

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Introduction

The European Union is fostering cleaner energy to make the EU a global leader in renewable energy and ensure that the target of at least 27% of renewables in the final energy consumption in the EU by 2030 is met. In this sense, the renewable gases such as biogas and hydrogen can play an important role to make the natural gas networks greener. In this sense Naturgas Energía has been collaborating with Tecnalia on the development of membranes that can surpass the current limitations today present, more precisely, the application of CMSM in the projects BioHysis (Hybrid and flexible system for biogas upgrading for injection in natural

Paper:

IBP0739 17

gas grid) and HyGrid (Flexible hybrid separation system for H_2 recovery from natural gas grid).

The BioHysis project for biogas upgrading

The BioHysis project proposes an integral solution for developing of an advanced high performance, cost effective separation technology biogas upgrading for its later injection in the natural gas network. For this purpose, novel CMSM membranes based on commercial polymers where developed showing better performance than state of the art membranes.



CMSM preparation procedure.

MEMBRANE FABRICATION



CMSM. a) Ceramic support. b) ceramic support with polymeric solution. c) and d) CMSM membrane [1] and [2]



solution containing 4% of PEI

PERMEATION TEST OF CMSM

Hydrogen and nitrogen permeation using single gas at various temperatures were carried out in the equipment reported before [3].



Gas flux of CO₂, CH₄ and N₂ at 35 and 100° C at various pressures of a supported membrane prepared from a dipping solution containing 4% of PEI and carbonized at 550° C.

Robeson upper bond plot for CO_2/CH_4 of the c-CMSM at 35 and 100°C, containing 4% PEI carbonized at 550°C

The HyGrid project. Flexible hybrid Separation System for H₂ Recovery from Natural Gas Grids



Conclusions

✓ CMSM are versatile membranes that have higher permeation properties than polymeric membranes and are able to surpass the Robeson plot limits. \checkmark In the BioHysis project, CMSM prepared from PEI show high permeation and selectivity towards CO₂ than methane and can be used for biogas upgrading. The

permeation in CMSM increases with temperature.

 \checkmark In the HyGrid project, AI-CMSM and Pd/Ag silver membranes will be developed for H₂ recovery from natural gas grids, promising results are being obtained.

References

[1] LLOSA TANCO, M.A., PACHECO TANAKA, D.A., RODRIGUES, S., MENDES, A. Composite- alumina-carbon molecular sieve membranes prepared from Novolac resin and Boehmite. Part I: Preparation, characterization and gas permeation studies. Int. J. Hydrogen. Energy, v. 40, n. 16, p. 5653-5663, 2015. [2] LLOSA TANCO, M.A., PACHECO TANAKA, D.A. Recent advances on carbon molecular sieve membranes (CMSMs) and reactors. Processes, v. 4, n. 3, p. 29, 2016. [3] MELENDEZ, J., FERNANDEZ, E., GALLUCCI, F., VAN SINT ANNALAND, M., ARIAS, P., PACHECO TANAKA, D. A. Preparation and characterization of ceramic supported ultra-thin ($\sim 1 \mu m$) Pd-Ag membranes. J. Membr. Sci., v. 528, p. 12-23, 2017.

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