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Effect of syngas composition on hydrogen permeation through a Pd–Ag membrane

Filomena Pinto *, Rui Neto André, Carlos Franco, Carlos Carolino, Ibrahim Gulyurtlu

LNEG, Estrada do Paço do Lumiar 22, 1649-038 Lisboa, Portugal

HIGHLIGHTS

- ► Effect of CH_4 and CO presence in syngas composition on membrane performance.
- ► Experimental conditions optimisation for H_2 permeation through a Pd–Ag membrane.
- ► H_2 permeances calculation.
- ► Activation energies between 11.5 and 14.0 kJ mol^{-1} were calculated.

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ABSTRACT

Hydrogen separation from a syngas mixture with different compositions was studied by using a Pd–Ag membrane. The effect of temperature (from 300 °C to 600 °C) and of relative pressure (from 0.2 MPa to 0.5 MPa) was studied. In general, rises of both these parameters allowed increasing H_2 permeate flux. The Pd–Ag membrane showed to have a great selectivity, as when inlet gas mixture contained different compositions of CO_2, CO or CH_4, these gases were never detected in membrane permeate side. However, when hydrogen content in inlet gas decreased, a significant reduction in H_2 permeate flux was observed, especially when CO was present, probably due to the deposition of solid carbon in membrane surface by Boudouard reaction. It was also observed the formation of hydrocarbons, due to CO and H_2 reactions. H_2 permeances were calculated by application of Sieverts' law and values between 4.9×10^{-4} and 1.5×10^{-3} mol m^{-2} s^{-1} Pa$^{-0.5}$ were obtained. The highest value was obtained at 600 °C. H_2 permeances at different temperature followed Arrhenius' equation. Thus, activation energies values between 11.5 kJ mol^{-1} and 14.0 kJ mol^{-1} were calculated.

1. Introduction

IEA predicts that the world's energy demand will continue to increase, due to the growth of world population and to the increasing needs in life quality. IEA estimates that world's energy demand would increase around 55%, between 2005 and 2030 [1]. Thus, it is expected that carbon dioxide (CO_2) emissions will continue to grow, mainly in developing countries. As CO_2 is a greenhouse gas, probably responsible for climate change, CO_2 emissions from energy production have to be limited. Hence, clean coal technologies, particularly carbon capture and storage (CCS) are most needed, especially in countries where coal use is growing faster.

Pre-combustion capture or gasification is a possible option to attain carbon capture before fuel combustion, by producing a hydrogen rich fuel and a CO_2 stream for storage. Oxy-gasification avoids the dilution effect of nitrogen and simplify CO_2 separation process. Syngas main components are: CO, CO_2 and H_2, especially after syngas cleaning processes to remove particulates, tar, NH_3, H_2S and HCl. After CO conversion into CO_2 by water gas-shift (WGS) reaction, the final syngas components are mainly H_2 and CO_2, which may be separated into a H_2 stream for energy production, while CO_2 flow goes to storage. Pure hydrogen demand has been increasing, due to its use in several industrial processes and to its potential use as a fuel, including in fuel cells. There are four major possible processes for H_2 and CO_2 separation: chemical or physical absorption, adsorption, cryogenic separation or membrane separation. These processes are at different stages of development and demonstration and all of them have limitations. The choice of the separation technology should consider syngas composition, operating temperature and pressure and process cost.

Chemical or physical absorption using solvents is a well known process, but it has a low efficiency and has a negative environmental impact, as huge amounts of solvents have to be circulated and regenerated and large equipments are needed. There are also high heat losses, great energy consumption and high solvent degradation rates. The main advantage of cryogenic separation is that liquid CO_2 is easier to transport, but normally this process has high

* Corresponding author. Tel.: +351 21 092 4787.
E-mail address: filomena.pinto@lneg.pt (F. Pinto).

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