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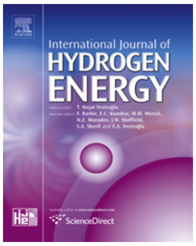

Technical Communication

# Bench-scale WGS membrane reactor for $CO_2$ capture with co-production of $H_2$

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ABSTRACT

This study investigated the water-gas shift reaction in a bench-scale membrane reactor (M-WGS), where three supported Pd membranes of 44 cm in length and ca. 6 μm in thickness were used, reaching a total membrane surface area of 580.6 $cm^2$. The WGS reaction was studied with the syngas mixture: 4.0% CO, 19.2% $CO_2$, 15.4% $H_2O$, 1.2% $CH_4$ and 60.1% $H_2$, under high temperature/pressure conditions: $T = 673$ K, $p_{feed} = 20–35$ bar(a), $p_{perm} = 15$ bar(a), mimicking $CO_2$ capture with co-production of $H_2$ in a natural gas fired power plant. High reaction pressure and high permeation of Pd membranes allowed for near complete CO conversion and $H_2$ recovery. Both the membranes and the membrane reactor demonstrated a long-term stability under the investigated conditions, indicating the potential of M-WGS to substitute conventional systems.

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## 1. Introduction

The increase in $CO_2$ emissions from fossil use has led to a great amount of research in the field of development of power plant equipped with $CO_2$ capture and storage (CCS). These will be able to produce electricity while the $CO_2$ produced is captured and stored in underground geological formations [1]. Several conventional and advanced technologies for $CO_2$ capture are being proposed. Compared to conventional capture technologies, the integrated $H_2$ membrane reactor shows significant potential advantages, such as lower capital investment, compactness, and lower energy consumption [2]. The membrane water-gas shift reactor can be incorporated in integrated gasification combined cycle (IGCC) or natural gas combined cycle (NGCC) power plant equipped with pre-combustion $CO_2$ capture. Here the energy content of the fuel is transferred towards hydrogen with $CO_2$ becoming available in a separate stream. The $H_2/CO_2$ separation required can be conducted with hydrogen separating membranes, which can be combined with carrying out the water-gas shift reaction for conversion of CO with $H_2O$ into $H_2$ and $CO_2$. Then, the equilibrium is shifted towards the product side due to the selective removal of $H_2$ and meanwhile the $CO_2$ rich stream can be retained on the other side of the membrane [3].

Special demands on membranes for use in pre-combustion $CO_2$ capture are: sufficient selectivity, high permeation flux, operability at high temperature (623–723 K). Also high

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pressure (approx. 22–25 bar) is important as the hydrogen fuel should be delivered at a pressure suitable for entering the gas turbine combustion chamber [4,5]. Among the inorganic membranes meeting the above requirements, the dense Pd or Pd-alloy membranes on a ceramic or metallic support are the most developed membrane types [5]. Through incorporating Pd membranes in the WGS reaction, high CO conversion exceeding equilibrium limit has been reported in the last decades [6–13]. For example, a CO conversion beyond 90% was attained by incorporating a 60 μm thick Pd–Ag membrane tube in a WGS reactor at 593 K and 6 bar(a) ($p_{\text{feed}}$), always exceeding the traditional reactor [12]. A maximum CO conversion of 98.6% was observed by Bi et al. [10] through a supported Pd membrane of 1.4 μm thick at 623 K and $p_{\text{feed}}/p_{\text{perm}}$ pressure of 12/1 bar(a), which was beyond the equilibrium value of 91%. It is worth mentioning that Basile et al. [13] achieved an almost complete CO conversion (99.9%) at a feed pressure of 1.2 bar and 595 K through a 0.2 μm thick Pd/ã-$A1_2O_3$/á-$A1_2O_3$ membrane reactor, i.e. considerably mild operating conditions, revealing the dramatic advantage of membrane reactor over a conventional reactor.

However, the present research on WGS Pd-based membrane reactor still remains at a lab-scale as reviewed by Basile et al. [14], and there are very few long-term stability tests of WGS membrane reactor reported. Moreover, these researches are mainly focused on $H_2$ production for industrial processes, such as ammonia synthesis, methanol synthesis, or fuel cell applications [14], while mostly investigated under low temperature/pressure conditions, i.e. between 523 K and 623 K [9,12,13] and below 12 bar(a) [9–13]. Therefore the next step in the development of membrane WGS technology comprises up scaling the membrane reactor, testing at realistic operating conditions and particularly improving the long-term stability of both the membranes and the membrane reactor.

This study will investigate for the first time the WGS reaction in a bench-scale membrane reactor under relevant conditions for $CO_2$ capture i.e. at 623–723 K and pressure up to 25 bar. Three long Pd membrane tubes will be used, reaching a total membrane surface area of 580 cm$^2$ and thus exceeding the lab-scale setup by orders of magnitude. A long-term stability of both the membranes and the membrane reactor will be provided.

## 2. Experimental

### 2.1. *Membrane preparation and characterization*

The membrane preparation process has been described in the previous paper [15]: first a commercial α-$Al_2O_3$ macroporous membrane support tube (ca. 500 mm long, o.d. = 14 mm) was tailored by suspension film coating two additional microporous 45 μm α-$Al_2O_3$ layers in ECN (Energy research Centre of the Netherlands) [16], and then a thin Pd layer was deposited in DICP (Dalian Institute of Chemical Physics, Chinese Academy of Sciences) by a modified electroless plating method [17]. Three Pd compositae membranes with a Pd layer thickness of 5.6–6.1 μm that have been previously used in the WGS-mixture separation test [15] were employed in this WGS reaction test after filling with noble metal shift catalyst (commercial, granulated substrate) within the annular zone, as they showed a stable $H_2$ permeance and a good $H_2/N_2$ selectivity of 330 at 673 K after the separation test.

### 2.2. *Permeation measurement*

The permeation apparatus PDU (Process Development Unit) has been described previously [15]. The mole-based WGS composition chosen in the test program was the same as in the WGS-mixture separation test [15], which represented the reformate gas from an oxygen-fed autothermal reformer followed by a shift reactor (623 K equilibrium shifted): 4.0% CO, 19.2% $CO_2$, 15.4% $H_2O$, 1.2% $CH_4$ and 60.1% $H_2$ [18]. The WGS reaction was carried out at 673 K with the feed pressure ranging from 20 bar(a) to 35 bar(a) and the permeate side fixed at 15 bar(a). The total feed gas flow rate was set between 30 NL/min and 90 NL/min with the sweep flow was fixed at 19.6 NL/min $N_2$. The base case was defined as a feed/permeate pressure of 31/15 bar(a) and a feed/sweep flow rate of 90/19.6 NL/min. No sweep gas was used during the measurement of pure $H_2$ and $N_2$ permeance while for the other measurements $N_2$ sweep gas was used in counter-current model.

The gas flow rate was measured by flow meters (Bronkhorst, F-112AC and F-113AC) while the composition of the retentate and permeate gas was monitored by an online gas chromatograph (HP, P200H) equipped with a mol sieve column, a poraplot column and a TCD detector. In addition, an advanced optima online analysis (ABB Magnos106) was also used to monitor the concentration of CO and $H_2$ with a Caldos 4T-EX detector. Permeation rates were measured after steady-state fluxes had been achieved.

## 3. Results and discussion

### 3.1. *Pure $H_2$ permeance*

Fig. 1 shows the pure $H_2$ permeance of the three membranes, which was measured at 673 K and with the $\Delta p$ gradually ranging from 1 bar to 5 bar. A high pure $H_2$ permeance of $2.5 \times 10^{-6}$ mol/m$^2$.s.Pa was measured at a feed/permeate pressure of 2.1/1 bar(a) for the three membranes of 5.6–6.1 μm thick, which is closely related to the modified electroless plating method [17]. The pure $H_2$ permeance decreased gradually with increasing feed pressure and pressure difference until it levelled off at feed pressures above 21 bar(a). This corresponds to an increase of $n$ value from 0.67 at feed pressures below 21 bar(a) to 0.94 at feed pressures above 21 bar(a), i.e. an increasing deviation from Sieverts' law [19]. It implies that the surface process dominates the $H_2$ permeation [20] at feed pressures above 21 bar(a). Morreale et al. [21] have also reported an increase of $n$ value from 0.50 to 0.62 at 623–1173 K for 1000 μm thick palladium disks with increasing the maximum pressure from 1.75 bar(a) to 27.6 bar(a), which was ascribed to the changes in the diffusion coefficient and Sieverts' constant at elevated pressures. However, the reason for the increase of $n$ value with increasing feed pressure is not fully understood yet, and requires to be further examined in future. Notably, a decreasing trend of pure $H_2$ permeance was

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