INHIBITION AT HIGH TEMPERATURES ON A PALLADIUM SILVER MEMBRANE FOR HYDROGEN SEPARATION

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Dream it. Do it.
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<thead>
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<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>Am</td>
<td>Pre exponential exponent of permeance</td>
</tr>
<tr>
<td>BOE</td>
<td>Barrel of oil equivalent</td>
</tr>
<tr>
<td>BPR</td>
<td>Back pressure regulator</td>
</tr>
<tr>
<td>(C_{H_2})</td>
<td>Concentration of hydrogen</td>
</tr>
<tr>
<td>d</td>
<td>Diameter of the membrane</td>
</tr>
<tr>
<td>D</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>(E_a)</td>
<td>Activation energy of hydrogen in the palladium-alloy membrane</td>
</tr>
<tr>
<td>F</td>
<td>Total flow rate</td>
</tr>
<tr>
<td>(F_{H_2})</td>
<td>Hydrogen flow rate</td>
</tr>
<tr>
<td>(F_{N_2})</td>
<td>Flow rate of nitrogen</td>
</tr>
<tr>
<td>(G^{an})</td>
<td>Function of (R_2)</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GDP</td>
<td>Gross domestic product</td>
</tr>
<tr>
<td>(J_M)</td>
<td>(H_2) flux</td>
</tr>
<tr>
<td>(K_S)</td>
<td>Sieverts constant</td>
</tr>
<tr>
<td>MDEA</td>
<td>Mono-diethanol ammine</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MFM</td>
<td>Mass flow meter</td>
</tr>
<tr>
<td>MRs</td>
<td>Membrane reactors</td>
</tr>
<tr>
<td>(P_C)</td>
<td>Critical pressure</td>
</tr>
<tr>
<td>(P_{H_2})</td>
<td>Partial pressure of hydrogen</td>
</tr>
<tr>
<td>PEM</td>
<td>Polymer electrolyte membrane</td>
</tr>
<tr>
<td>Perm</td>
<td>Permeate</td>
</tr>
<tr>
<td>Q</td>
<td>Permeability</td>
</tr>
<tr>
<td>(Q_M)</td>
<td>Membrane permeance</td>
</tr>
<tr>
<td>(R_1)</td>
<td>Radius of the membrane</td>
</tr>
<tr>
<td>(R_2)</td>
<td>Radius of the inner tube</td>
</tr>
<tr>
<td>Ret</td>
<td>Retentate</td>
</tr>
<tr>
<td>(Sh)</td>
<td>Sherwood number</td>
</tr>
<tr>
<td>SP</td>
<td>Set point</td>
</tr>
<tr>
<td>SR</td>
<td>Steam reforming</td>
</tr>
<tr>
<td>(t)</td>
<td>Thickness of the membrane</td>
</tr>
<tr>
<td>(T_C)</td>
<td>Critical temperature</td>
</tr>
<tr>
<td>Wt.</td>
<td>Weight</td>
</tr>
<tr>
<td>WT</td>
<td>Water separator</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>WGS</td>
<td>Water gas shift</td>
</tr>
<tr>
<td>(y_{H_2})</td>
<td>Molar fraction of hydrogen</td>
</tr>
<tr>
<td>(y^*_{H_2})</td>
<td>Sweep relative mole fractions</td>
</tr>
<tr>
<td>&lt; (y_{H_2}) &gt;</td>
<td>Average mole fraction</td>
</tr>
<tr>
<td>(y_w)</td>
<td>Wall mole fraction</td>
</tr>
</tbody>
</table>
ABSTRACT (English)

The effect of competitive adsorption on hydrogen permeation through a 75 \( \mu m \pm 1 \mu m \) Pd-Ag (~23%) membrane has been evaluated by means of comparisons between experimental and predicted data at temperatures of 350-500 °C and total pressure 2-10 barg. Predicted data were obtained by solving a mathematical model without taking into account external mass transfer resistance on hydrogen permeation thanks to the design of the tube where the membrane is fixed. This experimental work was done in the Chemical Engineering faculty at the Israel Institute of Technology.

At first, pure hydrogen was inserted into the system in order to measure the permeance of the membrane and at 500 °C it was 10.1760 \( \frac{m^3}{m^2\cdot bar\cdot s} \). Afterwards, hydrogen and nitrogen were inserted into the system and, as many other papers in the literature acknowledge, nitrogen was found to be inert: the reason for which the flow rate of hydrogen decreased was due to depletion and dilution. Then methane was inserted with nitrogen, and hydrogen to evaluate its effect on the membrane and no competitive adsorption was encountered. Soon thereafter, steam, nitrogen, and hydrogen were evaluated to check if water inhibited the membrane, but also in this case no reduction of hydrogen flow rate was found. Eventually, experiments with hydrogen, water, and methane were conducted. This was the most crucial part of the procedure because in other papers it was found that methane and water, even without a catalyst, could actually react on the surface of the membrane and create carbon monoxide, which is known to inhibit the palladium alloy membrane. However, no carbon monoxide was found and the hydrogen flow rate did not vary.

As a last experimental study a gas mixture of hydrogen, helium, and carbon monoxide was considered at two different temperatures, 350 and 500 °C at a feed pressure of 2 bar. Knowing from literature that at higher temperatures no inhibition occurs, the results at 500 °C were compared to the results at a lower temperature, 350 °C. No gas inhibition was found, concluding that on this specific membrane no inhibition takes place at high temperatures with different gas mixtures.
ABSTRACT (Italian)

Lo scopo del lavoro di ricerca svolto presso i laboratori del Dipartimento di Ingegneria Chimica della Facoltà Israel Institute of Technology è stato quello di capire se ad alte temperature varie miscele di gas potessero inibire la membrana di 75 μm ± 1 μm palladio-argento (~23%) nell’ambito della separazione dell’idrogeno ad alte temperature. La prima fase ha previsto la realizzazione di un impianto sperimentale per il rilievo di caratteristiche di permeabilità a gas di membrane tubolari in grado di operare a temperature di 350–500 °C e pressioni fino a 10 barg.

Inizialmente idrogeno puro è stato introdotto all’interno del sistema per capire la permeanza della membrana, e a 500 °C era $10.1760 \left[ \frac{m^3}{m^2 \cdot h \cdot bar^{0.5}} \right]$. In seguito, sono stati introdotti idrogeno e azoto ed è stato verificato che azoto sia un inerte: le cause della riduzione della portata d’idrogeno nel permeato sono dovute alla diluizione ed esaurimento. Poi metano, azoto, e idrogeno sono stati valutati come carica d’alimentazione e nessun effetto di adsorbimento da parte del metano sulla membrana è stato riscontrato. Successivamente, azoto, idrogeno, e vapore d’acqua sono stati introdotti nel sistema per capire se acqua inibiva la membrana, ma nessuna riduzione della portata di idrogeno è stata trovata. Come ultimo caso gli esperimenti sono stati fatti con idrogeno, metano, e vapore d’acqua. Questa era la parte cruciale dello studio perché altri lavori di letteratura riportano che metano ed acqua, senza la presenza di un catalizzatore, possono reagire sulla superficie della membrana creando monossido di carbonio che è in grado di inibire la membrana. Tuttavia, nessuna presenza di monossido di carbonio è stata trovata e nessuna riduzione della portata d’idrogeno è stata verificata.

Come ultimo studio, una miscela di gas d’idrogeno, elio, e monossido di carbonio è stata considerata a due temperature differenti, 500 e 350 °C alla pressione di 2 bar. Sapendo dalla letteratura che, ad alta temperatura non c’è inibizione dovuta a monossido di carbonio, i risultati a 500 °C sono stati confrontati con quelli a 350 °C: nessuna inibizione è stata trovata chiarendo che su questa specifica membrana non c’è inibizione ad alte temperature.
1 Introduction

1.1 Supply and Demand of Hydrogen

In the last decades, the world population has experienced a significant growth along with increasing energy demands and it will continuously grow as shown in Figure 1.1. The dependency on fossil fuels and the foreseen depletion of the world reserves in a near future are among of the biggest concerns.

![World Population: 1950-2050](image)

*Figure 1.1 – Estimation of population in the future (US Census Bureau, 2015).*

According to the United States Energy Information Administration, the world production of primary energy has increased in the last years. As it is clear from Figure 1.2, oil, natural gas, and coal (which aggregates peat and oil shale) represent most of the primary energy produced.
The consumption of energy is not uniform in the world: North America and Saudi Arabia consume the most and Russia follows. It is clearly shown in Figure 1.3 that most of the world has a lack of energy consumption: gross domestic product is proportional to energy consumption as reported in Figure 1.4.
Figure 1.4 – Gross domestic product versus total energy consumption (APS Physics, 2011).

Gross domestic product (GDP) is the monetary value of all the finished goods and services produced within a country’s border in a specific time period. The barrel of oil equivalent (BOE) is a unit of energy based on the approximate energy released by burning one barrel (42 U.S. gallons or 158.9873 liters) of crude oil. The BOE is used by oil and gas companies in their financial statements as a way of combining oil and natural gas reserves and production into a single measure, although this energy equivalence does not take into account the lower financial value of energy in the form of gas.

Dependency on fossil fuels, increasing greenhouse emissions, global warming, and other environmental concerns, are triggering the search for new and clean energy sources.

Hydrogen is claimed as the secondary energy or even a permanent solution to global-environmental problems, however it is not a primary energy source, rather an energy vector. It is also used in electricity, transportation, industrial, residential and commercial sectors as a fuel and/or an energy carrier. Other uses include hydrogenation of edible oils to produce margarine as well as metallurgical applications. For industrial demands, they are mainly in petroleum refining, production of ammonia, alcohols and Fisher-Tropsch hydrocarbons (*i.e.* gasoline, paraffins and light olefins, *etc.*) as seen in Figure 1.5.
Recent researches focus on hydrogen applications to fuel cells. Hydrogen can be produced from primary energy source such as solar, nuclear, fossil fuels (i.e. naphtha cracking and natural gas conversions), and electrolysis from water as it is shown in Figure 1.6.

Between 1980-2000, over 89% of hydrogen supply in the US refineries was from naphtha catalytic reforming, while other supplementary H₂ production plants gradually substituted it. Now, however, methane steam reforming is the most popular production method. Hydrogen production from natural gas became popular since the investment in a natural
gas-based plant is about one-third (or even less) of that required for a coal-based syngas plant.

1.2 Gas Production Synthesis from Methane Conversion

In recent years, hydrogen has gained much research emphasis as an energy carrier due to its environmental friendliness and wide range of energy applications. Approximately 95% of the hydrogen in the United States is generated via methane steam reforming. In addition to the maturity of the technology, natural gas reforming is also the most economical among all hydrogen production pathways. Methane steam reforming is a well-established process, as shown in Figure 1.7, steam and hydrocarbon enter the reactor as feedstock, and hydrogen and carbon dioxide are generated at the end of the process.

The process is governed by the reactions:

\[
CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{(298K)} = 206 \text{ kJ/mol} \quad (1)
\]

\[
CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_{(298K)} = -41 \text{ kJ/mol} \quad (2)
\]

\[
CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad \Delta H_{(298K)} = 165 \text{ kJ/mol} \quad (3)
\]

The steam-forming step, where methane reacts with water to produce carbon monoxide and hydrogen, is an endothermic process. Thus, the process is usually maintained at approximately 850 °C to obtain a desirable conversion. The second step is known as the water-gas shift reaction where syngas reacts to recover hydrogen. Conventionally, the process is performed in multi-tubular fixed-bed reactors in the presence of a metal catalyst.
However, the overall reaction is limited as both the steam reforming and the water-gas shift reactions are subjected to thermodynamic equilibrium. In the recent years, research has been devoted to the use of catalytic membrane reactors in overcoming the equilibrium limitation.

The use of steam reforming unit mitigates the problems of storage and distribution of hydrogen tanks for hydrogen vehicles. In addition, methane steam reforming operates at the highest efficiency compared to other current commercially available hydrogen production methods, such as partial oxidation of heavy oil and coal as well as coal gasification, however it requires high capital and operating costs in handling excess steam on corrosion problems. It is also not suitable for offshore or remote small-deposit application. Unfortunately, the production of hydrogen using steam reforming of natural gas does not eliminate greenhouse gas emissions. However, the carbon dioxide release is in fact lower for fuel cell vehicles powered by natural gas when comparing to those powered by gasoline.

### 1.3 Hydrogen Production in Membrane Reactors

Membranes and membrane reactors for pure hydrogen production are widely investigated not only because of the important application areas of hydrogen, but especially because mechanically and chemically stable membranes with high perm-selectivity (membrane selectivity) towards hydrogen are available and are continuously further improved in terms of stability and hydrogen flux. Membranes are basically barriers that allow the flow of some components of a feed gas mixture stream. The stream containing the components that permeate through the membrane is called permeate and the stream containing the retained components is called retentate. Membrane reactors are (multiphase) reactors integrating catalytic reactions (generally reforming and water gas shift reactions for hydrogen production) and separation through membranes in a single unit. This combination of process steps results in a high degree of process integration/intensification, with accompanying benefits in terms of increased process or energy efficiencies and reduced reactor or catalyst volume. An example of increased efficiency is the conversion of raw materials into hydrogen and its use in fuel cells. In fact, for example, in automotive applications electromotor combined with hydrogen-powered fuel cells show an overall efficiency (40–55%) significantly higher than internal combustion engines (13–30%). Platinum (Pt) based catalysts are commonly used in polymer electrolyte membrane (PEM) fuel cells. The performance of the catalyst decreases dramatically if carbon monoxide (a main product of most of the conversion technologies) or hydrogen sulfide are present. For this reason, the
interest in the production and separation of ultra-pure hydrogen has strongly increased in last years.

As mentioned above, traditionally, hydrogen is produced via steam reforming (SR) of hydrocarbons such as methane, naphtha oil, or methanol/ethanol. However, on industrial scale most of the hydrogen (more than 80%) is currently produced by steam reforming of natural gas carried out in large multi-tubular fixed-bed reactors. In small-scale applications, two other main alternatives are generally considered along with SR: partial oxidation reactions, with a significantly lower efficiency than SR, and auto-thermal reforming, where the partial oxidation (exothermic reaction) and SR (endothermic reaction) are carried out in the same reactor.

The main drawbacks of conventional SR, partial oxidation and auto-thermal conventional reactors are that all these reactions are equilibrium-limited and produce a hydrogen rich gas mixture containing carbon oxides and other by-products (even in case of complete fuel conversion). Consequently, in order to produce pure hydrogen, these chemical processes are carried out in a number of reaction units (typically high temperature reformer, high and low temperature shift reactors) followed by separation units (mostly pressure swing adsorption). The large number of different process steps decreases the system efficiency and makes scale-down uneconomical.

Among different technologies related to production, separation, and purification of H$_2$, membrane technologies seem to be the most promising and membrane separation is nowadays increasingly considered as a good candidate for substituting conventional systems. The specific thermodynamic constrains limiting traditional reactors can be circumvented by using innovative integrated systems, such as the so-called membrane reactors (MRs), engineering systems in which both reaction and separation are carried out in the same device, Figure 1.8.
In comparison to a conventional configuration in which a reactor is combined with a downstream separation unit, the use of membrane reactors can bring various potential advantages such as reduced capital costs (due to the reduction in size of the process unit), improved yields and selectivity (due to the equilibrium shift effect) and reduced downstream separation costs (separation is integrated).

The success of membrane reactors for hydrogen production depends crucially on:

(i) The advances in the membrane production methods for the production of thin membranes with high hydrogen fluxes and high hydrogen perm-selectivity.

(ii) The design of innovative reactor concepts, which allow the integration of separation and energy exchange, the reduction of mass and heat transfer resistances and the simplification of the housing and sealing of the membranes.

A Pd-based membrane leads to the following main benefits:

**a) A strong reduction of the reaction temperature**

Steam reforming reactions are very fast on Ni-based catalyst and quickly reach equilibrium conditions, leading to the necessity of increasing temperature to obtain a higher conversion. By integrating a selective membrane able to separate a reaction product as H\(_2\), the equilibrium conditions are not reached and this allows the promotion of the reactions at lower temperatures (450–650 °C), with the following advantages:
Higher efficiency of the heat transfer from the external source to the reactor.
Lower heating costs.
Use of cheaper alloy steel.

b) Increase in Process Efficiency
The lower temperature results in an increase of overall process efficiency, since the heat supplied is better exploited. It is foreseen that the global process efficiency should increase from the 65–80% of today’s technology up to 85% and more for all the plant sizes.

c) Large Saving of Methane
Reduction of reaction temperature means that the heat duty requirement is lower than for the traditional process. The heat flux from the external source to the catalytic bed should be about 30–40 kW m\(^{-2}\) instead of 80 kW m\(^{-2}\) and more of the traditional process: a smaller amount of methane has to be burned.

d) Reduction of CO\(_2\) Emissions
The methane saving leads to a reduction of the greenhouse gas emissions, since less or no carbon dioxide is produced by the methane combustion.

e) Easier CO\(_2\) Purification
Membrane integration into the reaction environment ensures a first substantial hydrogen separation step (up to 90% of the hydrogen produced can be removed); as for CO\(_2\) separation, because of the higher carbon dioxide partial pressure in the reformer outlet stream, due to the hydrogen removal, physical separation methods could be used to separate CO\(_2\) rather than the chemical adsorption in mono-diethanol ammine (MDEA).

f) Reduced Dependence on the Cost of Natural Gas
Increasing the reaction efficiency and reducing the amount of methane to be burned to supply the process heat duty requirements lead to a reduction of the total amount of methane required for producing a mass unit of hydrogen. Therefore, although a higher plant cost has to be supported because of the increasing reactor complexity, the hydrogen price would be less dependent on the natural gas.
1.4 Hydrogen Separation Applying Membranes

Different processes, such as cryogenic distillation, pressure swing adsorption, or permeation, can fulfill gas separation. Cryogenic distillation can reach high recoveries and good separations, but also demands high-energy consumption and is very expensive. Pressure swing adsorption, on the other hand, is able to deliver high purity compounds, but with really low recoveries. A simpler and versatile alternative technology is based on gas separation through membrane permeation. Membranes are compact and light weighted, which allows small units with reduced assembling costs. In addition, this technology can be coupled with a reaction unit, combining reaction and separation in the same device. Figure 1.9 shows a general classification scheme for membranes:

![Membrane classification](image)

**Figure 1.9 – Membrane classification (Iaquaniello et al., 2011).**

1.4.1 Organic Membranes

Polymer membranes can be divided in porous (high permeability and low selectivity) and dense membranes (low permeability and high selectivity).

One of the main drawbacks of these membranes is the selectivity of the polymer to high temperatures and aggressive chemical environments. Additionally, polymers can be swollen or plasticized when exposed to low concentrations of hydrocarbons or carbon dioxide.

1.4.2 Inorganic Membranes

Gas separation with inorganic membranes such as carbon, glass, or silica membranes is based on a molecular sieving effect through small pores.
Concerning the hydrogen separation from a gas mixture, amorphous silica membranes can present high hydrogen permeability and selectivity, but are not easy to produce without defects.

Glass membranes present low hydrogen fluxes and are extremely fragile. On the other hand, they show good thermal stability and chemical resistance. Zeolite membranes do not present high hydrogen selectivity due to pinholes and voids between zeolite crystals.

Carbon molecular sieve membranes are promising candidates for gas separations, due to their separation properties and high temperature resistance.

Figure 1.10 illustrates H₂ permeability through different metals: although niobium (Nb), vanadium (V), and tantalum (Ta) offer higher hydrogen permeability than palladium in a temperature range between 0 and 700 °C, however, these metals give a stronger surface resistance to hydrogen transport than palladium. These refractory metals (e.g., vanadium, niobium, and tantalum) have much higher permeability at lower temperatures in comparison to palladium: they are much cheaper and have greater tolerances to high temperatures compared to palladium. Nevertheless, producing membranes with only these metals (as pure components) is hindered by the high embrittlement produced at room temperature in presence of hydrogen. On the contrary, several alloys of these metals are also non-embrittling, making them good candidates for hydrogen purification membranes. These metals are not normally used alone for hydrogen permeation also because of poor surface properties (particularly formation of surface oxide layers) that reduce hydrogen transport: for this reason dense palladium membranes are preferentially used.

![Graph of Hydrogen Permeability through Different Metals](image1)

Figure 1.10 – Hydrogen permeability through different metals (Iaquaniello et al., 2011).
Palladium-based membranes are very popular for hydrogen separation due to their high selectivity towards hydrogen. The separation of \( H_2 \) shifts the reactions towards the products and allows reducing the operating temperature required for high conversions, while supplying pure hydrogen in one step. It also shifts the equilibrium towards \( CO_2 \) rather than \( CO \). The transport mechanism is based on the adsorption of hydrogen on the palladium surface, diffusion of the atomic hydrogen through the metal and recombination at the other side of the membrane. The main disadvantages of palladium-based membranes are the high prices and poisoning by sulphur and chlorine containing species, carbon monoxide, and water vapor and strongly adsorbing hydrocarbons. These membranes are usually used in temperatures such as 200-500 °C, but ultra-thin Pd membranes can operate at lower temperatures. However, these membranes suffer from mechanical instabilities such as easy peeling from the support material and defect formation due to hydrogen embrittlement. This is why palladium alloys are used rather than pure palladium membrane: palladium hydride phase transition may compromise membrane integrity to reduce surface poisoning by specific gas phase species, and to further enhance both the hydrogen transmembrane flux and the mechanical properties, finally the embrittlement is reduced. Membranes consisting of alloys of palladium-copper (Cu) and palladium-gold (Au) have received attention because these alloy systems offer some sulfur resistance. Hydrogen permeation results for a Pd-Au membrane show that this alloy exhibits better resistance to bulk sulfidation as compared to the Pd-Cu alloy system. Sulfidation is a chemical reaction of a solid substance, such as a metal or an alloy, with sulfur in some form in its working environment. This produces compounds of sulfur that usually form on the solid surface or under the surface of the substance, such as a metal or alloy. Sulfidation most often causes serious deterioration of the solid surface and the vital functional properties of the affected substance. Although the hydrogen flux is reduced up to 80% in presence of \( H_2S \), the permeance could nearly be fully recovered after a temperature increase, indicating that only reversible surface site blocking causes the poisoning of the Pd-Au alloy membrane. The absolute value of the permeability for these alloys, however, are low compared to that found in, for instance, Pd-23% Ag. The palladium-silver (Ag)(~23% wt. Ag because the hydrogen solubility has been found to be 10 times higher than for pure Pd) alloy membrane is probably the popular choice due to its high permeability and resistance to embrittlement below 300 °C. It is well known that hydrogen generally follows a solution–diffusion mechanism. The steps involved in hydrogen transport from a high to a low pressure gas region are the following: (a) Diffusion of molecular hydrogen to the surface of the metal membrane; (b) Reversible dissociative adsorption on
the metal surface; (c) Dissolution of atomic hydrogen into the bulk metal; (d) Diffusion of atomic hydrogen through the bulk metal; (e) Association of hydrogen atom on the metal surface; (f) Desorption of molecular hydrogen from the surface; (g) Diffusion of molecular hydrogen away from the surface.

When the diffusion of the atomic hydrogen through the metal bulk of the membrane is the rate-determining step and the hydrogen concentration in the palladium-based lattice is low enough, the Sieverts law should be valid, which relates the \( \text{H}_2 \) flux, \( J_m \), to the difference between the square roots of the \( \text{H}_2 \) partial pressures on the retentate and the permeate sides, Eqn. (4). The proportionality factor, \( Q_M \), is known as the membrane permeance and depends on the membrane composition, thickness, and temperature.

\[
J_m = Q_M(T) \sqrt{P_{\text{retentate}}^{\text{H}_2} - P_{\text{permeate}}^{\text{H}_2}} \quad (4)
\]

1.5 Instability of Palladium-Based Membranes

The most important problem associated with the use of pure palladium membranes is the ‘hydrogen embrittlement’ phenomenon. When the temperature is below 300 °C and the pressure below 2.0 MPa, the b-hydride phase may nucleate from the a-phase, resulting in severe lattice strains so that a pure palladium membrane becomes brittle after a few cycles of \( a \leftrightarrow b \) transitions. Such a problem can be overcome by using Pd-alloys containing another metal, such as silver. The palladium alloys have a reduced critical temperature for the \( a \leftrightarrow b \) phase transition. Pd-Ag membranes can operate in hydrogen atmosphere at temperatures below 300 °C without observing embrittlement rather than pure palladium membranes.

By alloying Pd with different elements, the phase transition can be suppressed, and in
particular alloys with 20–30 wt.% Ag or 40 wt.% Cu have been frequently investigated as membranes. Ag alloys have higher hydrogen permeability than pure Pd (up to about 70%), while Cu alloys have about the same. Palladium has also been alloyed with other metals, including ruthenium (Ru), gold (Au), yttrium (Y), nickel (Ni), iron (Fe) to obtain increased permeability, greater mechanical strength, inhibition of undesired grain growth, or enhancement of the resistance against poisoning of CO or sulfur-containing species. The majority of the works related to Pd-based membranes are on the highly permeable Pd-Ag alloy. The drawback is, however, that these alloys are prone to poisoning by CO and sulfur containing gases leading to reduced permeability because, for instance, CO reduces the flux due to competitive adsorption on the membrane surface, and thereby displaces hydrogen.

As an adsorptive effect: its importance increases with decreasing temperature and membrane thickness. The extent to which this affects stability and flux depends on many parameters, and the reported literature appears only partly consistent in this respect. The hydrogen streams to be purified usually contain several impurities, which can interact with the membrane surface in different ways. Understanding the nature of these interactions is fundamental to analyze the membrane behavior and correctly model the permeation process, which leads to a better design of the separation/purification modules. With respect to Pd-based membranes, but, also, more generally, to other types of metal membranes, all the non-permeating gas species (all gases except hydrogen) can be basically divided into the following two groups:

- Species adsorbing on metal surface so weakly that they do not affect the intrinsic membrane permeability. Therefore, these species are commonly regarded as inert species (*e.g.*, nitrogen (N₂) on palladium).

- Species that interact more strongly with the metal surface. This type of interaction, which is competitive with that of hydrogen, causes a decrease of the effective membrane area, because of the consequent reduction of the adsorption sites. The species behaving in this way are usually regarded as inhibiting or poisoning species (*e.g.*, CO, CO₂, or H₂S on palladium).

However, the analysis of these interactions is made more complicated by the fact that all the non-permeating species, *i.e.* inert, inhibiting/poisoning ones, are also responsible of a reduction of driving force along the permeation direction. This phenomenon, well known in membrane technology, is termed ‘concentration polarization’ and is generally caused by an
accumulation of the less-permeating species to the membrane surface due to the motion of
the more-permeating ones towards the membrane surface. The overall negative effect on
membrane performances is that the permeation driving force between the membrane
surfaces of upstream and downstream is lower than that between the respective bulks,
causing a consequent reduction of flux. A significant presence of concentration polarization
can make the advantages of preparing very thin membranes partially useless, because the
mass transfer resistance tends to be located in the gas phase external to the membrane
rather than in the membrane itself.
2 Thesis Objective

Objective of this thesis is to evaluate the permeability of a 75 μm Pd-Ag (~ 23%) membrane for hydrogen separation at different conditions. Scope of this study is not to probe the mechanism of the different gas mixtures on hydrogen permeation in detail, but to examine what extent (if any) these species have on hydrogen permeation through a Pd-Ag membrane under various operating conditions (temperature, concentration, etc.).

First of all modeling was done considering other literature and then experiments were performed. The experiments consisted of evaluating the flow rate of hydrogen through the membrane using, at first pure hydrogen to evaluate the permeance of the membrane, and then different gas mixtures were inserted into the experimental system: the goal was to understand if these gas mixtures inhibited the membrane at high temperatures (> 350 °C) compared to other experimental studies.

As a last consideration, different compositions of carbon monoxide were also inserted to evaluate if on a 75 μm palladium silver membrane, CO could adsorb on the palladium surface: carbon monoxide usually reduces hydrogen flux and flow rate.
3 Literature Review

3.1 Hydrogen production and separation through palladium-silver membranes

A large number of studies can be found in the scientific literature regarding reactor membrane technology with palladium/palladium-silver membranes. When hydrogen is introduced in a mixture with other gases, several effects may occur: (1) hydrogen depletion along feed flow direction, *i.e.* reduced hydrogen partial pressure and hence driving force for permeation, due to the selective removal of hydrogen; (2) in case of gas phase mass transport limitations, a buildup of a hydrogen-depleted layer adjacent to the membrane surface may occur (concentration polarization effect); (3) If other gas species adsorb on the surface, they may block hydrogen dissociation (competitive adsorption). Among the species expected in SR to cause permeance inhibition, CO is demonstrated to exert the most significant inhibition with respect to its bulk concentration, while CH₄ and CO₂ have a minor effect. Abir and Sheintuch (2014) studied the inhibition of Pd and Pd-Ag membranes by co-adsorbates. Their calculations show strong inhibition by CO, but methane adsorption was found to be negligible at temperatures of 330–530 °C, assuming either dissociative or associative adsorption. Still, several groups demonstrated that while CH₄ and H₂O show a negligible inhibition of the Pd membrane, a mixture of the two would have a much stronger inhibitive effect. Jung *et al.* (2000) found a hydrogen flux decline of ~50% at 500 °C when fed with H₂/CH₄/H₂O, compared to feed of H₂/CH₄. Inhibition of SR and WGS components (CO, CO₂, CH₄, H₂O) was investigated by Li *et al.* (2010) who found ~20% drop in H₂ flux relative to N₂/H₂ mixture with the same H₂ concentration. Israni *et al.* (2010) investigated the effect of methanol reforming species on hydrogen flux across Pd–Ag membrane, and found 80–90% decrease in flux due to adsorption of different species. They also concluded that CO has the strongest inhibition effect. They calibrated the various adsorption coefficients and suggested a proper expression for the available surface coverage of H₂. Most of the results in the literature are obtained for relatively high concentrations of H₂. Patrascu and Sheintuch (2014) made an onsite production of pure hydrogen by steam reforming in a high flux membrane reactor. The measurements were done in a membrane methane reformer packed with catalytic foams and equipped with a 175 cm² Pd membrane with a layer of 5 micron. This showed that high conversion and high recovery can be achieved at
temperatures around 500 °C with sweep flow and high pressure. However, the measured values of pure hydrogen were much lower in absence of reaction. The permeance inhibition was attributed to co-adsorbates and a possible reaction on the surface to create monoxide, due to the presence of methane and water, which is the most inhibitor, competitive adsorbent. Peters et al. (2007) evaluated the hydrogen permeation and stability of tubular palladium alloy (Pd–23%Ag) composite membranes and investigations on the flux behavior for a unique combination of high pressure (up to 26 bar) and very thin Pd–23%Ag composite membranes (~2 μm) were made. Differentiation was made between different rate limiting processes such as (i) dilution of hydrogen by other gas components, (ii) hydrogen depletion along the membrane length, (iii) concentration polarization adjacent to the membrane surface, (iv) the effects due to surface adsorption, on the hydrogen flux. Mejdell et al. (2009) estimated hydrogen permeation through thin (~3μm) palladium-silver membrane employed in a micro-channel membrane configuration. CO and CO_{2} showed an inhibitive effect on hydrogen permeation. The CO effect was strongly dependent on both temperature (275–350 °C) and CO concentration/partial pressure (0–5 mol%). The CO inhibition occurred rapidly upon exposure, with a sharp drop in flux between 0 and 0.25 mol% CO. CO desorption hence was the main mechanism for flux restoration at the higher temperatures. Yang et al. (2006) studied hydrogen permeance and surface states of Pd-Ag/ceramic composite membranes. Temperatures varied between 773 K and 553 K with different gas mixtures: CO_{2}, CH_{4}, CO, and H_{2}S were evaluated and the results respected the expectations: monoxide inhibits the membrane and hydrogen sulfide poisons it. Also Hou et al. (2001) estimated hydrogen permeation and inhibitors in Pd-Ag membranes at low pressure and temperature in between 548-723 K. Other than confirming that CO is the most inhibitor (at lower temperatures), the paper showed that the presence of steam reduces the hydrogen permeance. Kurokawa et al. (2014) evaluated the effect of carbon monoxide on the hydrogen permeability on a 12.5 micron-thick Pd/Ag membrane. While the CO inhibition effect was close to negligible at 500 °C, it was significant at lower temperatures. The results were then compared with other papers and the differences are conflicting. Barbieri et al. (2011) also tried to understand and evaluate inhibition by concentration polarization and competitive adsorption by experimental work and by also considering a permeation reduction coefficient, which helped to model the system.
3.2 Derivation of Sieverts law and Modifications

Hydrogen-permeable metal membranes are extraordinarily selective being extremely permeable to hydrogen but essentially impermeable to all other gases. The gas transport mechanism is the key to this high selectivity. Hydrogen permeation through a metal membrane is believed to follow the multistep process illustrated in Figure 1.11. Only hydrogen is transported through the membrane by this mechanism; all other gases are excluded. If the sorption and dissociation of hydrogen molecules is a rapid process, then hydrogen flux follows Sievert’s law, Eqn. (4). However, Eqn. (4) is correct only if bulk diffusion is the rate-limiting step. At sufficiently reduced thickness other processes, such as surface reaction rates or gas phase diffusion, may control the hydrogen permeation, which typically results in a change of the exponential coefficient of the partial pressure of hydrogen. A modeling study has concluded that bulk diffusion is expected to be the main rate-controlling step for pure palladium membrane thicknesses down to 1 μm above 300 °C. Experimentally, with hydrogen only used as feed gas, bulk diffusion was reported as rate limiting for 1 μm. Other researchers have, however, reported that surface reaction rate limitation becomes important already at higher thicknesses. Depending on the combination of Pd-membrane properties and operation conditions, different rate limiting processes may prevail. The processes commonly discussed are bulk diffusion and surface reaction. For a particular membrane the rate of bulk transport depends on membrane thickness, while the combination of surface characteristics and operation condition determines the rate of the surface reaction. Reduced hydrogen permeation rate due to surface effects is usually explained also by blocking of hydrogen surface sites by strongly adsorbing species, e.g., CO. The extent of permeation reduction is therefore a function of the composition, temperature, pressure, and the thickness of the employed membrane. Generally, in the presence of adsorbing gas components, the lower the temperature, and thinner the membrane employed, the more significant the hydrogen flux is affected by surface reaction. When the rate-limiting step is hydrogen diffusion through palladium membrane, the H₂ flux is obtained by the integration of Fick’s law:

\[ J_m = -D \frac{dC}{dt} = \frac{D}{t} \left( C_{H_2,1} - C_{H_2,2} \right) \]  

(5)

Where \( D \) is the diffusivity of hydrogen in the palladium membrane, which is assumed to be independent of the hydrogen concentration (m² s⁻¹), \( t \) is the thickness of the membrane (m),
and \(C_{\text{H}_2,1}, C_{\text{H}_2,2}\) are the hydrogen concentrations in the palladium membrane in equilibrium with the feed and permeate gas, respectively (mol m\(^{-3}\)).

These concentrations can be expressed as:

\[
C = \xi \eta \quad (6)
\]

Where \(\xi\) is the hydrogen concentration constant (mol m\(^{-3}\)) and \(\eta\) is the atomic H/Pd ratio, which is a function of temperature and hydrogen partial pressure. At low concentrations of hydrogen, \(\eta\) is linearly dependent on the square root of partial pressure of hydrogen, giving:

\[
P_H^{0.5} = K_S \eta \quad (7)
\]

\(K_S\) is the Sieverts constant. Combining equations above:

\[
J_m = \frac{D (\xi/K_S)}{t} \left( P_{\text{H}_2,1}^{0.5} - P_{\text{H}_2,2}^{0.5} \right) \quad (8)
\]

In which the term \(\xi/K_S\) represents the hydrogen solubility, \(S\), in the palladium layer. The product of the diffusivity, \(D\), and solubility, \(S\), is often referred to as the hydrogen permeability, \(Q\). Thus, if diffusion through the membrane is rate limiting, Sieverts law gives the hydrogen flux as

\[
J_m = \frac{Q}{t} \left( P_{\text{H}_2,1}^{0.5} - P_{\text{H}_2,2}^{0.5} \right) \quad (9)
\]

However, at sufficiently reduced thickness, other processes may control the hydrogen permeation and the Sieverts law becomes more general:

\[
J_m = \frac{Q}{t} \left( P_{\text{H}_2,1}^n - P_{\text{H}_2,2}^n \right) \quad (10)
\]

Where \(n\) is between 0.5 and 1 and its value has to be found experimentally.

### 3.3 Membrane Inhibition

In membrane separation processes, a gas or liquid mixture contacts the feed side of the membrane, and a permeate enriched in one of the components of the mixture is withdrawn from the downstream side of the membrane. Because the feed mixture components permeate the membrane at different rates, there is a gradual build-up in the concentration of non-permeating or slowly permeating components in the feed as the more permeable components pass through the membrane.

A layer is formed near the surface of the membrane, whereby the solution immediately adjacent to the membrane surface becomes depleted in the permeating solute on the feed side of the membrane, and its concentration is lower than that in the bulk fluid. On the other hand, the concentration of the non-permeating component increases at the membrane.
surface. A concentration gradient is formed in the fluid adjacent to the membrane surface. This phenomenon is known as concentration polarization and it serves to reduce the permeating component’s concentration difference across the membrane, thereby lowering its flux and the membrane selectivity.

Depletion, together with dilution, is a reason for a minor reduction of hydrogen through the membrane. Hydrogen dilution on the feed side is due to the presence of other gas components, and hydrogen depletion of the bulk feed is due to hydrogen removal along the length of the membrane module. The build-up of a hydrogen-depleted layer adjacent to the membrane surface is possible for to gas phase mass transport limitation. In the following figure it is possible to evaluate the impact of the major inhibition factors. Figure 3.1 illustrates the expected flux reduction due to dilution, depletion, and concentration polarization as a function of the total feed pressure.

Figure 3.1 – Impact of inhibition factors on the hydrogen flux (Peters et al. (2007)).
4 Experimental Setup

4.1 Permeance Measurements

In order to evaluate the permeation behavior of the Pd-Ag membrane, various feeds were used as permeation gasses, including pure hydrogen and mixed feed of hydrogen with nitrogen, methane, and steam. Permeance was measured in the experimental system, Figure 4.2 and Figure 4.3, which incorporates feed, membrane reactor, and an analysis section. It is important to remember that in this particular experimental study no reaction in the gas phase took place, but only hydrogen permeation in different gas mixtures at high temperatures was evaluated. An American company, REB, provided the membrane. The palladium-silver (\(~23\%\) wt.) membrane is a foil wrapped on coil supported on Inconel 600 with a thickness of \(75 \mu m \pm 1\mu m\). Inconel is a family of austenite nickel-chromium-based super-alloys. Inconel alloys are oxidation and corrosion resistant materials well suited for service in extreme environments subjected to pressure and heat.

It is 3.2 mm in outer diameter and 0.25m in effective length and it has an effective area for hydrogen separation \(~25\) cm\(^2\).

Three identical concentric electric heaters from the outside heat the shell, and each heater is controlled independently to maintain a set temperature. Three additional thermocouples are located inside the membrane in order to measure the temperature. Figure 4.1 is a real picture of the membrane configuration: it is easily visible the heaters and the thermocouples on the outside. Inside the heaters there is a thick aluminum tube, which has the crucial task to protect the membrane; thanks to its high conductivity all heat goes directly to the inner tube where the membrane is fixed and the gasses flow.

All gases were introduced into the membrane reactor by a calibrated mass flow controller (Brooks Inc.) and deionized water was pumped by a highly accurate metering diaphragm pump (Grundfos). Pressure differences across the membrane were obtained by varying the pressure of the retentate and maintaining the permeate at atmospheric pressure; pressure was controlled by a backpressure regulator (BPR, ITT industries) and water was taken out of the system by a water separator (WT).

Hydrogen embrittlement was not an issue thanks to the silver alloy, however temperatures were maintained at around 350 °C and above for experimental reasons. For permeation experiments with the mixed feed of hydrogen with other species, the latter were introduced
into the feed, with steam following the establishment of the initial hydrogen flow, and the permeation rate was measured once steady-state for hydrogen permeation was achieved. No sweep gas was used on the permeate side in all the permeation experiments. To eliminate any possible permanent effect of the other species on the membrane, the hydrogen permeability for the membrane was repeatedly measured with pure hydrogen feed between the mixed feed permeation experiments. Furthermore, the membrane was leak checked with nitrogen before and after every experimental procedure.

In the first part of the experimental studies pure hydrogen was fed to the retentate side of the separator (at specific temperatures and pressures) in order to determine the pure gas permeation properties of the membrane. In the second part of the experimental study H\(_2\), along with variable compositions of at least a second component, were fed to the retentate side. The effect of the other components on the hydrogen flux was investigated by substitution with N\(_2\) while keeping the H\(_2\) content constant. These feed compositions are based on other experimental studies.

The retentate was always sent to the analyzing system comprised of a gas chromatography (GC). Measurements of the permeate composition were conducted occasionally. All measurements verified that the permeate composition was >99.5% H\(_2\). Permeate flow is measured directly by a mass flow meter (MFM) (Alicat Scientific, Inc.). Permeate pressure is around atmospheric pressure in all experiments conducted in this study, however a 1.5 bar of pressure was assumed in all calculations.

In the last part of the experimental work, hydrogen along with carbon monoxide, and helium were introduced at high temperatures (>350 °C) to understand if inhibition due to CO competitive adsorption took place and then the experimental results were compared with other literature papers.
Figure 4.1 – The membrane configuration used in the system.
Figure 4.2 – PFD of the experimental setup.
Figure 4.3 – Experimental lab setup.
Figure 4.4 shows the detailed drawing of the membrane configuration. The outer section is the aluminum tube, whose function is to protect the membrane. The inner tube is where the gases flow and inside, represented in red, is the membrane. The feed flows from right to left. The hydrogen permeates inside the membrane and it flows through the membrane and heads out with 100% purity. The rest of the feed, with the hydrogen that did not permeate, leaves from the exhaust channel and leads toward the GC where the gas mixture is evaluated. Figure 4.5 is a representation of membrane configuration.

Figure 4.4 – Detailed drawing of the membrane configuration.

Figure 4.5 – Scheme of a Pd-based membrane permeator tube in tube-in-tube configuration (Caravella et al., 2010).
4.2 Instrumentation

The most important instrumentation used during the experiments is:

a) Gas chromatography  
b) Rotameter  
c) Mass flow control

a) Gas Chromatography

The gas chromatography used in the system is the Trace GC Ultra of the Thermo Scientific. GC is used to analyze compounds of the exhaust gas. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture, the relative amounts of such components can also be determined: in this case it was used to understand the relative amounts of components inside the flow.

In gas chromatography, the mobile phase, or “moving phase”, is a carrier gas: helium was used. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support and it is inside a piece of glass or metal tubing called column.

The gaseous compounds analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness.

Figure 4.6, represents a simple diagram of the GC configuration.
b) Rotameter

This instrument is placed in the system to have an evaluation of the flow rate and it is very useful during the experimentations to have an approximated flow rate of the exhaust gas and to understand when the system is stable after the manipulation of the pressure valve.

A rotameter, Figure 4.7, is a device that measures the flow rate of gas in a closed tube. It belongs to a class of meters called 'variable area meters', which measure flow rate by allowing the cross-sectional area the fluid travels through, to vary, causing a measurable effect.

A higher volumetric flow rate through a given area increases flow speed and drag force so the float will be pushed upwards. However, as the inside of the rotameter is cone shaped (widens), the area around the float through which the medium flows increases and the flow speed and drag force decrease until there is mechanical equilibrium with the float's weight of the float.
c) Mass Flow Control

A mass flow controller (MFC), Figure 4.8, is a device used to measure and control the flow of liquids and gases. A mass flow controller is designed and calibrated to control a specific type of liquid or gas at a particular range of flow rates. The MFC can be given a set point (SP) from 0 to 100% of its full-scale range but is typically operated in the 10 to 90% of full scale where the best accuracy is achieved: the device will then control the rate of flow to the given set point. MFCs can be either analog or digital. A digital flow controller is usually able to control more than one type of fluid whereas an analog controller is limited to the fluid for which it was calibrated: the one used in the lab was digital.
4.3 Calibration

Calibration is really important to understand the feed flow rate. The experimental system has three MFC: the first one for CH$_4$, the second for H$_2$, and the last for N$_2$. For every MFC the calibration curve was calculated. To achieve this result, the gas flows were inserted at a fixed pressure with different valve openings. This operation was repeated with different pressures to be sure that the calibration curve wouldn’t change. For nitrogen and methane the calibration curve was approximately the same at different pressures; however for hydrogen a change of curve was noticed: for this reason, depending on pressure, a different SP for each pressure was chosen. The reason for the different calibration curves for hydrogen is probably because the mass flow control isn’t able to control hydrogen that well and so there is a loss caused by different pressure: higher the pressure, harder it is the control the hydrogen and a corrector is needed to have the desired flow rate.

The curves and the equations achieved follow beneath:
Figure 4.9 – Calibration curve for methane.

Figure 4.10 – Calibration curve for hydrogen.
Figure 4.11 – Calibration curve for nitrogen.
5 Results and Discussion

5.1 Calculation of the diameter of the inner tube

Due to the objective of this experimental study, that is to evaluate inhibition on the Pd-Ag membrane due to different gas mixtures at high temperatures, it was imperative to neglect concentration polarization. Concentration polarization is present in all membrane processes, even though it has been neglected for a long time in the gas separation field. As mentioned in Chapter 3, this phenomenon occurs because the perm-selectivity of the membrane itself consists of a decrease in driving force of the most permeable species due to the presence of the least permeable ones. Its negative effect on membrane performances can be relevant when the selective layer is quite thin.

The first field for which concentration polarization was deeply investigated was liquid separation by membrane processes, such as ultrafiltration and reverse osmosis. On the contrary, for a long time it was generally accepted that concentration polarization has only a negligible effect on membrane performance in gas separation. This was justified by the fact that membranes were quite thick and permeating flux very low, and, moreover that gas diffusivities are four to five orders of magnitude higher than those of the liquids.

However, the progress obtained in the last few decades in membrane preparation for gas separation has allowed the transmembrane flux to be significantly improved. High permeating flux causes the external mass transfer to seriously affecting membrane performances, because a greater driving force tends to be concentrated out of the membrane and not in the selective layer. Peters et al. (2007) and Kurokawa et al. (2014) found that concentration polarization is the main effect of hydrogen flux reduction in many membrane reactors such as the famous Tokyo Gas reformer. Tokyo Gas developed the world's largest scale of membrane reformer with a rated H₂ production capacity of 40 Nm³/h for on-site hydrogen production from natural gas, achieving the world's highest hydrogen production efficiency of 81.4%. The obtained H₂ flux in the Tokyo Gas membrane reformer, however, equals only 50% or less of the flux values assuming bulk diffusion of hydrogen through the Pd membrane as rate determining. This reduction can tentatively be explained by membrane inhibition due to co-existing gases, or so-called concentration polarization, or a combination of both. However, as mentioned above, Kurokawa et al. (2014) concludes that the inhibition effect, in that particular case, of all the co-existing gas species, is negligible or extremely small.
and the flux reduction is due to concentration polarization caused by depletion of hydrogen in the gas-phase layer next to the membrane surface. This reduces the efficient partial pressure of hydrogen and thereby the pressure gradient sustaining the H₂ flux. These gas phase limitations can only be improved by smart membrane and module design in order to optimize feed flow conditions to reduce the thickness of the hydrogen-depleted layer.

For this reason, to start the experiments in the laboratory, it was necessary to evaluate the limiting diameter of the inner tube over which concentration polarization could be present. Figure 5.1 shows three different zones:

- Upstream side, were a multi-component gas mixture is present.
- Pd-based membrane, which is the actual selective layer responsible for separation.
- Downstream side, where only pure hydrogen is present.

Both forward and backward permeation are shown, however in this experimental study only hydrogen purifier (forward permeation) is considered; hydrogen supplier (backward permeation) can be found elsewhere.

![Figure 5.1 – Sketch of different zones in a membrane configuration (Caravella et al., 2010).](image)

To evaluate the diameter of the tube, Nekhamkina and Sheintuch (2015) were taken into consideration: the objective was to evaluate the maximum diameter over which concentration polarization cannot be neglected.

The paper describes approximated models to simulate the transmembrane hydrogen flux also in an empty membrane separator, which is the case study of this experimental work.
A parameter $\Gamma$, a dimensionless number, was identified which represents the ratio of diffusive to permeating flux. The average mole fraction, $<y_{H_2}>$, and the wall mole fraction, $y_w$, coincide at two limiting points:

- No membrane flux: $<y_{H_2}> = y_{H_2w} = y_{H_2}^*$
- Pure hydrogen flow: $<y_{H_2}> = y_{H_2w}$

Where $y_{H_2}^* = \frac{p_{H_2w}}{p_{ret}}$ is the sweep relative mole fractions.

Under the condition $y_{H_2}^* \ll y_{H_2w}$ (in the limiting case of a very high sweep velocity ($y_{H_2}^* \to 0$)), the species polarization, defined as a difference between the average and the wall values, depend on a single parameter $\Gamma$ that can be estimated \textit{a priori}. Figure 5.2 suggests that with $\Gamma > 6$ the wall mole fraction practically coincides with the average value, thus concentration polarization can be neglected. This theory was also validated by several experimental studies which confirmed that concentration polarization can be totally neglected if $\Gamma > 10$ and approximated to zero if $\Gamma > 6$.

\[
\Gamma = \frac{D \times Sh}{d \times \kappa \times \sqrt{p_{ret}}} \quad (11)
\]

$\kappa$ is the permeability coefficient in Sievert’s law divided by the total molar concentration in $cm/(s \ bar^{0.5})$.

$D$ is the diffusion coefficient measured in $cm^2/s$.

$p_{ret}$ is the pressure in the retentate in $bar$.

$Sh$ is the Sherwood number.

$d$ is the diameter of the membrane in $cm$.

<table>
<thead>
<tr>
<th>$\kappa \left[ \frac{cm}{s \ bar^{0.5}} \right]$</th>
<th>$D \left[ cm/s^2 \right]$</th>
<th>$p_{ret} \left[ bar \right]$</th>
<th>$d \left[ cm \right]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7333</td>
<td>0.3599</td>
<td>10</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The calculations were developed considering the limiting-case scenario of the experimental operation conditions: 500 °C and 10 bar. If concentration polarization were negligible then also at milder conditions the mass transport limitations could be approximated to zero.

The values of the parameters, Table 1, were obtained by considering the paper of Patrascu and Sheintuch (2014).
To evaluate the maximum diameter of the tube the Sherwood number, for an annular configuration, had to be found. In Nekhamkina and Sheintuch (2015), the Sherwood number is calculated as follows:

\[ Sh = \frac{(R_2 - R_1)^2 \times (R_2^2 - R_2^2)^2}{12 \times R_2 \times R_1 \times G^{an}(R_2)} \]  

(12)

Where:
- \( R_1 \) is the radius of the membrane.
- \( R_2 \) is the radius of the inner tube.
- \( G^{an} \) is a function of \( R_2 \) and equations (13-15) show the calculation procedure.

\[ G^{an}(R_2) = \frac{1}{2} [R_2 g^{an}(R_2) - \phi^{an}(r)] \]  

(13)

\[ g^{an}(r) = \int_{R_1}^{r} \frac{F^{an}(r)}{r} \, dr = \frac{R_2^2}{6} \left( 1 - \frac{R_2}{2R_1} \right) \ln \frac{r}{R_1} - \left( \frac{r^2}{4} - \frac{r^3}{9} \frac{R_1 + R_2}{R_1 R_2} + \frac{r^4}{16R_1 R_2} \right) \bigg|_{R_1}^{R_2} \]

(14)

\[ \phi^{an}(r) = \frac{R_2^2}{6} \left( 1 - \frac{R_2}{2R_1} \right) \frac{r^2}{2} \bigg|_{R_1}^{R_2} - \left( \frac{r^4}{8} - \frac{r^5}{15} \frac{R_1 + R_2}{R_1 R_2} + \frac{r^6}{24R_1 R_2} \right) \bigg|_{R_1}^{R_2} \]  

(15)

Furthermore, Eqn. (11) is a function depending only on the radius of the tube: this was plotted in Figure 5.3. In order to calculate the radius of the tube, Eqn. (11) was plotted by varying \( Sh \) (Eqn. (12)) from a radius of 0 cm until 10 cm. The Sherwood number is dimensionless and it represents the ratio of the convective mass transfer to the rate of diffusive mass transport.
Figure 5.2 – Effect of the parameter \( \Gamma \) on the hydrogen polarization showing the dependence of the wall fraction \( (y_w) \) on the averaged value \( (<y>) \) with a fixed value of sweep relative mole fraction \( (y^*) \) equal to zero. The thick dashed line marks the limiting case \( y_w = <y> \) (Nekhamkina and Sheintuch, 2015).

Figure 5.3 – The dimensionless number as a function of the radius of the inner tube.

As mentioned above, Nekhamkina and Sheintuch (2015) claimed that to be certain that there was not an effect of concentration polarization, gamma had to be more than six; from
Figure 5.3, it is visible that to have $\Gamma > 6$ a radius of $\sim 0.5 \text{ cm}$ is necessary and this value was used to build the tube.

Figure 5.4 is a representation in COMSOL software of a part of the inner tube: the space inside the tube is where the palladium silver membrane was fixed.

5.2 Experimental Results

Objective of this experimental study was to understand if different gas mixtures such as methane, water, and nitrogen, could inhibit the palladium silver membrane at high temperatures. Indeed, one of the main reasons for hydrogen permeation decrease is the possible competitive adsorption of the other species with hydrogen on the film surface. The main task, however, was to evaluate, on a thicker membrane, the hypothesis of Patrascu and Sheintuch (2014): surface steam reforming reaction on a Pd alloy membrane can occur in a gas mixture of methane and water.

In their paper a mathematical model predicts the performance of the reactor well in terms of axial temperature profile, exit compositions, and permeate flow when membrane permeance is calibrated with experimental results. However, this value is significantly lower ($\sim 80\%$) than values measured in pure hydrogen in absence of reaction. This apparent permeance inhibition is attributed to co-adsorbates. The concentration of CO, which is thought to be the strongest inhibitor, is less than 1\% and it cannot be the cause of the strong inhibition. To assess the permeance inhibition effect, due to co-adsorbates on the Pd surface, they predicted permeate flow for different cases: by assuming the equilibrium adsorption coefficient of CH$_4$ equal to that of CO, they found a good agreement with experiments at the
range of 1-15 bar. This is an important result because without considering the inhibition effect, one would increase H₂ production monotonically, so other considerations (e.g. mechanical, economical) would define the optimum pressure. However, co-adsorption inhibition of this type suggests that increasing the driving force for H₂ transport through the retentate pressure would be ineffective beyond a certain point.

Thus, if adsorption equilibrium is assumed, then to justify the strong inhibition, surface reaction of methane on the Pd membrane to form CO would explain the strong inhibition: the CO created would not be in equilibrium with the gas phase and would inhibit the membrane surface.

For this reason the following experimental procedure was followed:

- The first operation was to understand the permeance of the membrane and, to do so, pure hydrogen was inserted into the system.
- Nitrogen was then inserted into the system: considering other literature nitrogen should be an inert. In specific, the results were compared to Boon et al. (2012), which made many experimental operations only on hydrogen and nitrogen.
- Proceeding with the experiments, methane was inserted into the system with hydrogen, and nitrogen. Considering other literature, CH₄, at lower temperatures is considered almost as an inert.
- Then hydrogen, water, and nitrogen were introduced into the system. There are many different opinions on the effect of water. Many papers validated the fact that at all temperatures water, without the presence of methane, is in effect an inert; however, Hou et al. (2001) experimented the opposite.
- After considering separately how water and methane act with nitrogen, they were inserted together without the presence of a catalyst. In many papers WGS mixtures were considered and in all of them the effects were devastating for hydrogen flow. Even if in this specific case the gas mixtures do not consider carbon monoxide and carbon dioxide, water and methane could react, even without a catalyst, and create carbon monoxide, which has a huge inhibiting effect on the palladium silver membrane, as mentioned in Patrascu and Sheintuch (2014).

All experiment values were compared both to the simulations and to other papers; a one-dimensional equation was taken into account without considering concentration polarization, which was neglected (see Paragraph 5.1).
5.2.1 Pure Hydrogen

As mentioned above, in order to calculate the permeance of the palladium alloy membrane, only pure hydrogen was introduced in the experimental system. Permeance is defined as the ratio of the permeability coefficient to the membrane thickness. The permeability coefficient is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness and its value has to be experimentally determined.

The experiments consisted in changing the pressure from 2 to 8 barg at different temperatures, between 300 and 500 °C.

Taking in consideration Sievert’s law, Eqn. (4), and Eqn. (16), the permeance, \( Q_m \), was found by non-linear regression with the data reported in Table 2.

\[
Q_m = A_m \times \exp \left( \frac{-E_a}{R \times T} \right) \tag{16}
\]

Where \( A_m \) is the pre exponential factor and \( E_a \) is the activation energy of hydrogen in the palladium-alloy membrane.

The pre exponential factor, \( A_m \), was found to be around \( 0.45 \text{ [mol} \text{ m}^2 \text{ sec bar}^{-0.5}] \) and \( E_a \) around \( 10 \text{ [kJ mol}^{-1}] \).

The permeance at high temperatures (500 °C) was around \( 10.1760 \text{ [m}^3 \text{ m}^2 \text{ h bar}^{-0.5}] \). Other papers found slightly different results, (lower activation energy) probably because of the thinner thickness of their Pd-alloy membrane: \( \text{H}_2 \) permeance of a Pd alloy membrane is proportional to the inverse thickness of the dense membrane layer. It can be concluded that the membrane used in the present study showed similar performances and behavior compared to other membranes prepared by the same procedure, and the experiments were subsequently initiated.

Figure 5.5 shows permeability of pure hydrogen through the Pd-Ag membrane as the function of pressure difference at different temperatures. In all cases, hydrogen flux was proportional to the difference in the square root of pressure, indicating that this agreed with Sievert’s law (Eqn. (4)) and that the diffusion of hydrogen was indeed the rate-determining step in the membrane.

Figure 5.5 shows also how hydrogen flux slightly increases with temperature and it is justified by the relationship between permeance and temperature, Eqn. (16).
5.2.2 Hydrogen and Nitrogen

After evaluating the permeance of pure hydrogen, nitrogen was inserted into the system. In many papers nitrogen is put into the system because it is normally used as a dilution gas in the feed mixture in order to monitor the appearance of leakage through the membrane. It is generally accepted that for short periods of exposure, nitrogen gas has no or only very weak adsorption on Pd-alloy surface. At this step, different gas mixtures of nitrogen and hydrogen
were inserted into the system. However, with the ongoing of the experiments nitrogen was
gradually removed to insert other gas mixtures, leaving the hydrogen concentration
constant. By evaluating nitrogen and hydrogen feed, it was possible to understand the
dilution and depletion effect. These results were then compared to the other experiments,
where other gas mixtures are not always considered as inerts to the Pd-alloy membrane.
Indeed, if other gas mixtures inhibited more than nitrogen and hydrogen, then it would be
possible to conclude the inhibiting effect of that specific gas mixture.
Boon et al. (2012) investigated mass transfer limitations in supported palladium-based
membrane separators. To do so, only hydrogen and hydrogen and nitrogen were inserted
into their experimental system. They experimented the fact that in the radial direction,
concentration polarization strongly reduced the H₂ concentration at the membrane surface.
Secondly, as H₂ permeates through the membrane, the feed side becomes H₂ depleted as
evidenced from the decrease of average H₂ concentration with the axial position.
By neglecting concentration polarization in this study, no build-up of a hydrogen-depleted
layer adjacent to the membrane surface due to gas phase mass transport limitation should
be present (see also Paragraph 5.1). The only reason for the reduction in hydrogen flow rate,
in this experimental study, should be for dilution on the feed side by the presence of other
gas components and hydrogen depletion of the bulk feed due to hydrogen removal along the
length of the membrane module.
Two gas mixtures were considered:
• 50% of H₂ and 50% of N₂
• 30% of H₂ and 70% of N₂
To simulate the flow rate of hydrogen and nitrogen, a one-dimensional model was modeled
and to evaluate the composition of the retentate, the following differential equation was
considered:
\[
\frac{dF_{H_2}}{dz} = -\pi d Q m \sqrt{p_{ret}^{H_2}} - \sqrt{p_{perm}^{H_2}} 
\] (17)
Where \( F_{H_2} \) is the hydrogen flow rate.
The molar flow of hydrogen changes with its permeation through the membrane, so the
above becomes:
\[
\partial y_{H_2} = -\frac{(1 - y_{H_2})}{F} * P * d * \left( \sqrt{p_{per}^{H_2}} - \sqrt{P_0} \right) 
\] (18)
Where \( y_{H_2} \) is the molar fraction of hydrogen in the system, \( F \) is the total flow rate and it is equal also to \( F = F_{N_2}/(1-y_{H_2}) \), where \( F_{N_2} \) is the total flow rate of nitrogen.

In order to resolve the numerical equations, \textit{Matlab} was used and the following procedure was applied for every experimental study.

At first, by using the calibration equations discussed in Paragraph 4.3, the flow rates were obtained. Then temperature and pressure were set and the experimental values were inserted. Afterwards, the permeance was calculated at the specific temperature and the differential equation (Eqn. (18)) was calculated by using the function \textit{ode45} and by varying the membrane length from 0 to 25 cm and this was plotted with the experimental results. Subsequently, hydrogen flow rate (Eqn. (17)) was calculated by using the function \textit{trapz} and this was also plotted with the experimental results. This procedure was then repeated for every temperature, pressure and gas mixture.

Following are the experimental results, which they compared with the simulations.

For 400 °C and total flow rate of 1 L/min:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Gas mixture [H\(_2\):N\(_2\)]\% & Pressure permeate [bar] & Pressure retentate [barg] & Experimental permeate flow rate [L/min] & Calculated composition outlet retentate [%H\(_2\)] & GC composition [%H\(_2\)] \\
\hline
30:70 & 1.5 & 6 & 0.078 & 24.07 & 20.029 \\
30:70 & 1.5 & 8 & 0.101 & 18.20 & 19.162 \\
30:70 & 1.5 & 10 & 0.145 & 14.87 & 21.981 \\
50:50 & 1.5 & 6 & 0.178 & 37.61 & 38.30 \\
50:50 & 1.5 & 8 & 0.281 & 30.36 & 28.885 \\
50:50 & 1.5 & 10 & 0.333 & 24.88 & 29.97 \\
\hline
\end{tabular}
\caption{Experimental values at 400 °C and with a total flow rate of 1 L/min.}
\end{table}
For 500 °C and total flow rate of 1 L/min:

Table 4 – Experimental values at 500 °C and with a total flow rate of 1 L/min.

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>6</td>
<td>0.086</td>
<td>23.41</td>
<td>17.933</td>
</tr>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>8</td>
<td>0.154</td>
<td>17.33</td>
<td>25.380</td>
</tr>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>10</td>
<td>0.185</td>
<td>14.14</td>
<td>22.940</td>
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<tr>
<td>50:50</td>
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<td>6</td>
<td>0.204</td>
<td>37.07</td>
<td>35.980</td>
</tr>
<tr>
<td>50:50</td>
<td>1.5</td>
<td>8</td>
<td>0.292</td>
<td>29.28</td>
<td>29.651</td>
</tr>
<tr>
<td>50:50</td>
<td>1.5</td>
<td>10</td>
<td>0.344</td>
<td>23.62</td>
<td>23.050</td>
</tr>
</tbody>
</table>

Figure 5.6 – Decrease of the hydrogen composition in the retentate at 400 °C with 50%, H₂% & 50% N₂.
Figure 5.7 – Hydrogen flow rate in permeate side with 50% H₂ & 50% N₂ at 400 °C.

Figure 5.8 – Decrease of the hydrogen composition in the retentate at 500 °C with 50% H₂ % & 50% N₂.
Figures 5.6-5.9 show how the simulations and the experimental results are very similar for a gas mixture of 50% of hydrogen and 50% of nitrogen. The retentate stream was calculated by subtracting the hydrogen feed with the exit flow rate from the permeate side. The same experimental approach was investigated but with different gas mixtures: 30% of hydrogen and 70% of nitrogen.
Figure 5.10 – Decrease of the hydrogen composition in the retentate at 400 °C with 30% H₂ & 70% N₂.

Figure 5.11 – Hydrogen flow rate in permeate side with 30% H₂ & 70% N₂ at 400 °C.
Figure 5.12 – Decrease of the hydrogen composition in the retentate at 500 °C with 30% H₂ % & 70% N₂.

Figure 5.13 – Hydrogen flow rate in permeate side with 30% H₂ & 70% N₂ at 500 °C.

From the graphs above, it is noticeable that the simulation and the experimental results are different. For some reason the amount of hydrogen in the permeate is much greater than the expected one. At first, a fear of leakage in the membrane was thought. Secondly, a different
permeance was also considered, however this idea was then rejected due to the amazing correspondence between the simulations and the 50% H\textsubscript{2} & 50% N\textsubscript{2} gas mixtures. The reason of this big difference was not understood until an experimental evaluation was done with the same gas mixtures but with double flow rate: 2 L/min. With a double flow rate, the experimental results and the simulations are similar, which brought to the conclusion that with a gas mixture of 30% of hydrogen and 70% of nitrogen, and with a flow rate of 1 L/min, the experimental values are not precise due to a bad hydrogen control of the experimental system. However, it was also evaluated the fact that underneath a certain flow rate, higher quantity of hydrogen permeates due to the fact that there could be a relationship between permeance, flow rate and hydrogen concentration. However, this theory was subsequently rejected because after this experimental study, the mass flow control was controlled and then changed, and a 30% of hydrogen with 70% of hydrogen was re-evaluated and simulations were indeed similar to the experimental results. In the following experiments, for a mixture of 30% of hydrogen at 1 L/min, the results are compared to the simulations above, so a fair comparison could be evaluated. For 400 °C and total flow rate of 2 L/min:

<table>
<thead>
<tr>
<th>Gas mixture [H\textsubscript{2}:N\textsubscript{2}]%</th>
<th>Pressure permeate [bar]</th>
<th>Pressure retentate [barg]</th>
<th>Experimental permeate flow rate [L/min]</th>
<th>Calculated composition outlet retentate [%H\textsubscript{2}]</th>
<th>GC composition [%H\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>6</td>
<td>0.083</td>
<td>26.99</td>
<td>22.424</td>
</tr>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>8</td>
<td>0.144</td>
<td>24.61</td>
<td>20.120</td>
</tr>
<tr>
<td>30:70</td>
<td>1.5</td>
<td>10</td>
<td>0.192</td>
<td>22.63</td>
<td>19.950</td>
</tr>
</tbody>
</table>
Figure 5.14 – Decrease of the hydrogen composition in the retentate at 400 °C with 30% H₂ % & 70% N₂ with 2L/min.

Figure 5.15 – Hydrogen flow rate in permeate side with 30% H₂ & 70% N₂ at 400 °C.
In the tables above, respectively Table 3 & Table 4, there is sometimes a difference between calculated retentate composition and the composition revealed from the GC. This is probably because of the instability of the system and how the GC works. It is known that the GC takes into account only a sample of the flow in the system, so probably in the sample taken; the composition was slightly different than the expected one.

Below is an example of a chromatogram for 30% of hydrogen and 70% of nitrogen at 10 barg.

![Mass chromatogram for 30% of hydrogen and 70% of nitrogen (a).](image)
5.2.3 Hydrogen Methane and Nitrogen

Even if the best results were achieved with 2 L/min of flow rate, the experiments were continued with 1 L/min in order to have similar flow rates to other experimental systems. After verifying that nitrogen is an inert, methane was inserted into the system without changing neither the composition and the quantity of hydrogen or the total flow rate. CH₄, in other papers such as Peters et al. (2007) and Patrascu and Sheintuch (2014), shows almost no hydrogen flux inhibition. Investigations are carried out to verify this assumption also in this experimental study.

The gas mixtures considered were:

H₂:N₂:CH₄ → 30%: 46.6%: 23.3%.
H₂:N₂:CH₄ → 50%: 33.3%: 16.6%.

To simulate the flow rate, CH₄ was considered an inert and then compared with the exit flow rate of hydrogen. If CH₄ inhibited the membrane, the quantity of hydrogen in the outlet would be lower than the one expected.

Following are the simulations and experimental result for 50% of hydrogen, 33.3% of nitrogen and 16.6% of methane.

---

Figure 5.17 – Mass chromatogram for 30% of hydrogen and 70% of nitrogen (b).
For 400 °C and total flow rate of 1 L/min:

**Table 6 – Experimental values at 400 °C and with a total flow rate of 1 L/min with N₂, H₂, and CH₄.**

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.089</td>
<td>23.19</td>
<td>29.027</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.154</td>
<td>17.35</td>
<td>19.292</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>10</td>
<td>0.188</td>
<td>13.84</td>
<td>15.421</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
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<td>6</td>
<td>0.212</td>
<td>36.55</td>
<td>35.214</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
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<td>8</td>
<td>0.294</td>
<td>29.19</td>
<td>28.994</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>10</td>
<td>0.332</td>
<td>25.09</td>
<td>25.986</td>
</tr>
</tbody>
</table>

For 500 °C and total flow rate of 1 L/min:

**Table 7 – Experimental values at 500 °C and with a total flow rate of 1 L/min with N₂, H₂, and CH₄.**

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.090</td>
<td>35.89</td>
<td>31.394</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.145</td>
<td>28.27</td>
<td>27.202</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>10</td>
<td>0.193</td>
<td>23.25</td>
<td>24.218</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>6</td>
<td>0.220</td>
<td>23.10</td>
<td>25.732</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>8</td>
<td>0.303</td>
<td>18.22</td>
<td>23.951</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>10</td>
<td>0.348</td>
<td>13.31</td>
<td>21.555</td>
</tr>
</tbody>
</table>
Figure 5.18 – Decrease of the hydrogen composition in the retentate at 400 °C with 50% H₂ % & 33.3% N₂ & 16.6% CH₄ with 1L/min.

Figure 5.19 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% N₂ & 16.6% CH₄ at 400 °C.
Figure 5.20 – Decrease of the hydrogen composition in the retentate at 500 °C with 50% H₂ & 33.3% N₂ & 16.6% CH₄ with 1L/min.

Figure 5.21 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% N₂ & 16.6% CH₄ at 500 °C.
The evaluation is very simple: in these conditions methane acts like an inert and does not inhibit the membrane.

Peters et al. (2007) also considered CH₄ as in inert, at higher pressures and with a thinner Pd membrane, but only because it did not inhibit the palladium membrane as much as carbon monoxide and carbon dioxide; in this case study, methane does not vary the flow rate of hydrogen and it acts just like nitrogen.

This is verifiable also in the following graphs where 30% of hydrogen is inserted into the system. However, even if the simulations and the experimental results do not match, the graphs are similar to the ones above where a gas mixture of 30% of hydrogen and 70% of nitrogen is inserted at 1 L/min and for this reason it is reasonable to conclude that also with a higher concentration of methane, no inhibiting effect occurs.

![Graph showing hydrogen flow in membrane](image)

**Figure 5.22 – Decrease of the hydrogen composition in the retentate at 400 °C with 30% H₂ % & 46.6% N₂ & 23.3% CH₄ with 1L/min.**
Figure 5.23 – Hydrogen flow rate in permeate side with 30% H\textsubscript{2} & 46.6% N\textsubscript{2} & 23.3% CH\textsubscript{4} at 400 °C.

Figure 5.24– Decrease of the hydrogen composition in the retentate at 500 °C with 30% H\textsubscript{2} % & 46.6% N\textsubscript{2} & 23.3% CH\textsubscript{4} at 500 °C.
Figure 5.25 – Hydrogen flow rate in permeate side with 30% H₂ & 46.6% N₂ & 23.3% CH₄ at 500 °C.

Below is an example of a chromatogram for 50% of hydrogen, 33.3% of nitrogen, and 16.6% of methane at 8 barg.

Figure 5.26 – Mass chromatogram for 50% of hydrogen, 33.3% of nitrogen, and 16.6% of methane (a).
Hydrogen Water and Nitrogen

After noticing that methane in the operating conditions used in this experimental system was an inert, deionized water was inserted into the system. It was imperative to understand if water, between 350 and 500 °C at different pressures (2-10 barg), inhibited the membrane or it was also considered as an inert. In many papers, such as Patrascu and Sheintuch (2014), steam does not adsorb on the palladium membrane. However, Hou and Houghes (2001) investigated the effect of hydrogen on a palladium alloy membrane and experimented the fact that steam is indeed an inhibitor. In their experimental study a 5% of steam caused a 70% decrease of hydrogen permeation rate. The strong effect of steam addition, at around 300 °C and a pressure of 2 bar on a 4 μm Pd-Ag membrane, meant that steam had a very high adsorption capacity on the Pd-Ag surface, compared to other components such as CO and CO₂. This theory is contradictory to other papers in literature, and for this reasons this

![Figure 5.27 – Mass chromatogram for 50% of hydrogen, 33.3% of nitrogen, and 16.6% of methane (b).](image)

5.2.4 Hydrogen Water and Nitrogen

After noticing that methane in the operating conditions used in this experimental system was an inert, deionized water was inserted into the system. It was imperative to understand if water, between 350 and 500 °C at different pressures (2-10 barg), inhibited the membrane or it was also considered as an inert. In many papers, such as Patrascu and Sheintuch (2014), steam does not adsorb on the palladium membrane. However, Hou and Houghes (2001) investigated the effect of hydrogen on a palladium alloy membrane and experimented the fact that steam is indeed an inhibitor. In their experimental study a 5% of steam caused a 70% decrease of hydrogen permeation rate. The strong effect of steam addition, at around 300 °C and a pressure of 2 bar on a 4 μm Pd-Ag membrane, meant that steam had a very high adsorption capacity on the Pd-Ag surface, compared to other components such as CO and CO₂. This theory is contradictory to other papers in literature, and for this reasons this
The experimental study investigated the effect of steam at higher pressures, temperatures using a thicker membrane.

The gas mixtures considered in this experimental study were:

- H₂:N₂: H₂O → 30%: 23.3%: 46.6%
- H₂:N₂: H₂O → 50%: 16.6%: 33.3%

In order to verify the effect of water hydrogen, and nitrogen, methane was not inserted into the system. The amount of water into the system was not the same as methane in the previous case because the percentage of water and methane, in the last experimental study (Paragraph 5.2.5), will be the ones evaluated here and in Paragraph 5.2.3.

The water was pumped into the system by SMART Digital pump. At first, a calibration was made and then calculations were performed to understand how much water should be pumped into the system to have the right amount of water vapor in the system.

![SMART Digital pump](image)

Figure 5.28 – SMART Digital pump for water.

Considering the case of 46.6% of water, in normal conditions, so 1 bar and 25 °C (298 K), there are 0.0188 moles/min and knowing that there are 55.5 mol/L, it is necessary to have 20.5 ml/h pumped into the system. These calculations were repeated also for the latter case, where 33.3% of the gas mixture was water and the final result was to have 14.5 ml/h pumped.

Just like the experiment above, to simulate the flow rate, H₂O was considered an inert; if water did inhibit the membrane, the flow rate of hydrogen in the outlet would be lower than the one expected.
The main problem of this experimental study was that water was not pumped continuously into the system: every 3-4 min water would be pumped and for this reason hydrogen flow rate oscillated. Figure 5.29 represents how hydrogen flow rates changes when water is in inserted; instead Figure 5.30 is an example of how hydrogen flow is stable when water is not introduced into the system.

![Example of oscillations of hydrogen flow with water.](image)

![Example of hydrogen flow without water.](image)

For evaluation reasons, an average value was calculated to have a reference point for simulation reasons. Table 8 and Table 9 are the experimental values and following are the simulations and experimental results for 50% of hydrogen, 33.3% of water, and 16.6% of nitrogen.
For 400 °C and total flow rate of 1 L/min:

**Table 8 – Experimental values at 400 °C and with a total flow rate of 1 L/min with N\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O.**

<table>
<thead>
<tr>
<th>Gas mixture [H\textsubscript{2}:H\textsubscript{2}O:N\textsubscript{2}]%</th>
<th>Pressure permeate [bar]</th>
<th>Pressure retentate [barg]</th>
<th>Experimental permeate flow rate [L/min]</th>
<th>Calculated composition outlet retentate [%H\textsubscript{2}]</th>
<th>GC composition [%H\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.095</td>
<td>47.04</td>
<td>45.776</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.175</td>
<td>35.27</td>
<td>35.400</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>10</td>
<td>0.198</td>
<td>30.07</td>
<td>32.500</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>6</td>
<td>0.210</td>
<td>63.60</td>
<td>63.987</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>8</td>
<td>0.310</td>
<td>53.38</td>
<td>59.742</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>10</td>
<td>0.358</td>
<td>46.09</td>
<td>56.962</td>
</tr>
</tbody>
</table>

For 500 °C and total flow rate of 1 L/min:

**Table 9 – Experimental values at 500 °C and with a total flow rate of 1 L/min with N\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O.**

<table>
<thead>
<tr>
<th>Gas mixture [H\textsubscript{2}:H\textsubscript{2}O:N\textsubscript{2}]%</th>
<th>Pressure permeate [bar]</th>
<th>Pressure retentate [barg]</th>
<th>Experimental permeate flow rate [L/min]</th>
<th>Calculated composition outlet retentate [%H\textsubscript{2}]</th>
<th>GC composition [%H\textsubscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.094</td>
<td>55.39</td>
<td>43.490</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.175</td>
<td>43.11</td>
<td>42.361</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>10</td>
<td>0.202</td>
<td>37.20</td>
<td>39.786</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>6</td>
<td>0.225</td>
<td>62.36</td>
<td>64.049</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>8</td>
<td>0.325</td>
<td>51.33</td>
<td>58.466</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>10</td>
<td>0.375</td>
<td>42.84</td>
<td>56.027</td>
</tr>
</tbody>
</table>
Figure 5.31 – Decrease of the hydrogen composition in the retentate at 400 °C with 50% H₂, 33% H₂O & 16.6% N₂ with 1L/min.

Figure 5.32 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% H₂O & 16.6% N₂ at 400 °C.
Figure 5.33 – Decrease of the hydrogen composition in the retentate at 500 °C with 50% H₂ & 33.3% H₂O & 16.6% N₂ with 1L/min.

Figure 5.34 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% H₂O & 16.6% N₂ at 500 °C.

At these conditions it is possible to evaluate that water is an inert. This is a different result compared to Hou and Houghes (2001) where water did adsorb on the palladium surface.
However, the experimental results and the simulations are not as precise as the ones in the previous paragraphs. The main cause is due to the oscillation of the hydrogen flow rate during the experimental study; even if the results are not so accurate, it is possible to confirm that water is an inert on the palladium alloy membrane at high temperatures. This is verifiable also in the following graphs where 30% of hydrogen is inserted into the system with 46.6% of water and 23.3% of nitrogen. However, even if the simulations and the experimental results do not match, the graphs are similar to the ones above (Paragraph 5.2.2) where a gas mixture of 30% of hydrogen and 70% of nitrogen is inserted at 1 L/min.

![Graph showing decrease of hydrogen composition in the retentate at 400 °C with 30% H₂, 46.6% H₂O, and 23.3% N₂.](image)

**Figure 5.35** – Decrease of the hydrogen composition in the retentate at 400 °C with 30% H₂ & 46.6% H₂O & 23.3% N₂ with 1L/min.
Figure 5.36 – Hydrogen flow rate in permeate side with 30% H₂ & 46.6% H₂O & 23.3% N₂ at 500 °C.

Figure 5.37 – Decrease of the hydrogen composition in the retentate at 500 °C with 30% H₂ % & 46.6% H₂O & 23.3% N₂ with 1L/min.
Below is an example of a chromatogram for 30% of hydrogen, 46.6% of water, and 23.3% of nitrogen at 400 °C at the pressure of 8 barg. No steam is present in the chromatogram because after leaving the membrane reactor, steam became water again and was separated at the WT. The GC traced a small quantity of carbon dioxide because a very small leakage was found: this was fixed immediately.
5.2.5 Hydrogen Methane and Water

After noticing that also water was an inert, a new gas mixture was considered without changing the composition and the quantity of neither hydrogen nor the total flow rate. The main reason for this experimental study lies in this paragraph. Methane steam reforming reaction normally takes place at high temperatures by inserting, with water and methane, a nickel based catalyst. As specified at the beginning of this study, no reaction in the gas phase took place but only different gas mixtures were inserted into the system to verify their effect on the membrane surface. By inserting a fix quantity of methane, water, and hydrogen, a simulation of SR reaction is evaluated. The reason for which no carbon monoxide and carbon dioxide were inserted is because both gases are known to inhibit the Pd membrane. However, by simulating the outlet composition of Patrascu and Sheintuch (2014) without considering carbon monoxide and carbon dioxide, it was possible to verify if a thicker Pd-Ag membrane could actually react with methane and water to create enough quantity of carbon monoxide in order to inhibit the surface of the membrane; this
theory has not been evaluated in many other papers, especially not using a 75 $\mu m$ Pd/Ag membrane (thicker membranes than the new state of the art membranes which have a 3-4 $\mu m$ layer).

In the experiments of Patrascu and Sheintuch (2014), after reaction took place, not all of methane and water reacted. However, with methane and water, also hydrogen, carbon dioxide, and carbon monoxide were present at the outlet; for this reason in this study a higher quantity of hydrogen is present because it incorporates also the quantity of carbon monoxide and carbon dioxide.

The gas mixtures considered were:

$H_2$:$CH_4$: $H_2O \rightarrow 30\%: 23.3\%: 46.6\%$

$H_2$:$CH_4$: $H_2O \rightarrow 50\%: 16.6\%: 33.3\%$

The composition of methane and water was the same of the previous paragraphs (see Paragraphs 5.2.4 & 5.2.3). It was crucial to understand if methane and water, together, inhibited the membrane. To simulate the flow rate, $CH_4$ and $H_2O$ were considered as inerts. If this gas mixture inhibited the membrane, the quantity of hydrogen in the outlet would be lower than the one expected.

Following are the simulations and experimental result for 50% of hydrogen, 33.3% of water, and 16.6% of methane.

For 400 °C and total flow rate of 1 L/min:

<table>
<thead>
<tr>
<th>Gas mixture $[H_2:H_2O:CH_4]%$</th>
<th>Pressure permeate [bar]</th>
<th>Pressure retentate [barg]</th>
<th>Experimental permeate flow rate [L/min]</th>
<th>Calculated composition outlet retentate [%$H_2$]</th>
<th>GC composition [%$H_2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.080</td>
<td>48.67</td>
<td>49.383</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.145</td>
<td>40.17</td>
<td>37.840</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>6</td>
<td>0.198</td>
<td>64.40</td>
<td>72.469</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>8</td>
<td>0.270</td>
<td>57.95</td>
<td>57.199</td>
</tr>
</tbody>
</table>
For 500 °C and total flow rate of 1 L/min:

Table 11 – Experimental values at 500 °C and with a total flow rate of 1 L/min with CH₄, H₂, and H₂O.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>6</td>
<td>0.100</td>
<td>46.30</td>
<td>49.383</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>8</td>
<td>0.175</td>
<td>35.15</td>
<td>37.84</td>
</tr>
<tr>
<td>30:46.6:23.3</td>
<td>1.5</td>
<td>10</td>
<td>0.195</td>
<td>31.22</td>
<td>-</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>6</td>
<td>0.225</td>
<td>62.22</td>
<td>71.198</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>8</td>
<td>0.315</td>
<td>52.57</td>
<td>47.384</td>
</tr>
<tr>
<td>50:33.3:16.6</td>
<td>1.5</td>
<td>10</td>
<td>0.365</td>
<td>44.60</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 5.41 – Decrease of the hydrogen composition in the retentate at 400 °C with 50% H₂ % & 33.3% H₂O & 16.6% CH₄ with 1L/min.
Figure 5.42 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% H₂O & 16.6% CH₄ at 400 °C.

Figure 5.43 – Decrease of the hydrogen composition in the retentate at 500 °C with 50% H₂ & 33.3% H₂O & 16.6% CH₄ with 1L/min.
Figure 5.44 – Hydrogen flow rate in permeate side with 50% H₂ & 33.3% H₂O & 16.6% CH₄ at 500 °C.

From figures 5.41-5.44 it appears that at 400 °C there is a slight reduction of hydrogen flow rate than at 500 °C. It is known that at higher temperatures, carbon monoxide has more difficulty to adsorb on the palladium sites.

However, the composition of the retentate was then evaluated into the GC to evaluate the gas mixture: no CO was found. This result showed firstly that flow reduction was mainly due to the oscillations of hydrogen for the water pump (Paragraph 5.2.4). Secondly, it also neglected the fact that CO, on a 75 μm ± 1 μm membrane, was present. This result is contradictory towards Patrascu and Sheintuch (2014), which assumed that methane and water, when inserted into the system, did create carbon monoxide on the palladium surface, which inhibited the membrane. However, their result could have been correct because they used a thinner Pd membrane (3-4 μm) without a silver alloy.

This is verifiable also in the following graphs where 30% of hydrogen is inserted into the system with 46.6% of water, and 23.3% of methane. However, even if the simulations and the experimental results do not match, the graphs are similar to the ones above (Paragraph 5.2.2) where a gas mixture of 30% of hydrogen and 70% of nitrogen is inserted at 1 L/min
Figure 5.45 – Decrease of the hydrogen composition in the retentate at 400 °C with 30% H₂, 46.6% H₂O, and 23.3% CH₄ with 1L/min.

Figure 5.46 – Hydrogen flow rate in permeate side with 30% H₂, 46.6% H₂O, and 23.3% CH₄ at 400 °C.
Figure 5.47 – Decrease of the hydrogen composition in the retentate at 500 °C with 30% H₂ & 46.6% H₂O & 23.3% CH₄ with 1L/min.

Below is an example of a chromatogram for 50% of hydrogen, 33.3% of water, and 16.6% of methane at 500 °C and a pressure of 6 barg. No steam is present in the chromatogram.
because after leaving the membrane reactor, steam became water again and was separated at the WT.

Figure 5.49 – Mass chromatogram for 50% of hydrogen, 33.3% of water, and 16.6% of methane (a).

Figure 5.50 – Mass chromatogram for 50% of hydrogen, 33.3% of water, and 16.6% of methane (b).
6 CO Inhibition

6.1 The inhibition effect of carbon monoxide

The hydrogen concentration adjacent to the membrane surfaces and the number available of hydrogen adsorption sites on the surface are decisive factors for the hydrogen flux. One of the significant issues related to Pd-based membranes is the inhibition of the H₂ flux due to co-existing gas species adsorbing strongly on the membrane surface, for example, when membrane is applied for hydrogen separation from reformed gases composed of CO, CO₂, CH₄, and H₂O. Among these gases, CO is known as a major inhibiting species. The extent of the inhibition effect depends on the gas composition, temperature, pressure, and thickness of the membrane. In addition, the hydrogen flux is most affected at lower temperatures. It has been reported that one CO molecule can block different sites on Pd surface and that one single adsorbed CO molecule can block more than one hydrogen dissociation site. Consequently, a small concentration of CO could result in a remarkable decrease in hydrogen permeation, particularly for thin membranes where permeation is rate controlled by surface reaction processes.

Figure 6.1 shows the inhibition effect of CO on hydrogen permeation as a function of CO feed content at feed and permeate pressure equal to 0.2 and 0.15 MPa, respectively. The total feed flow rate was 1 L/min and hydrogen, carbon monoxide, and helium (helium is an inert) were inserted into the system. The reason for which also helium was considered is because only a gas tank with 92.5% of helium and 7.5% of CO was available for the experimental procedure. Every time the concentration of CO increased, also the quantity of helium increased: this meant that dilution and depletion had to be accounted for.

The results are plotted as relative hydrogen flow rate to allow for a direct comparison of the CO inhibition effect obtained at the different temperatures. The relative hydrogen flow rate corresponds to the measured flow rate in the presence of CO normalized by the flow rate obtained before introduction of CO under otherwise equal conditions of temperature, total absolute feed pressure, hydrogen partial pressure and total feed flow rate. The inhibition effect of CO on hydrogen permeation depends on both CO concentration and temperature, and increases with decreasing temperature and increasing CO concentration in the ranges applied. Moreover, the inhibition should level off upon saturation of the surface with increasing CO concentration, although saturation was not reached at the maximum CO
concentration of 3 vol.%. The CO inhibition effect was compared between 350 °C and 500 °C. In the scientific literature it is known that at high temperatures and relative thick membranes, CO does not inhibit the palladium silver membrane. However, at lower temperatures (350 °C) many papers in literature such as Peters et al. (2007), Mejdell et al. (2009), and Kurokawa et al. (2014) experienced a major decrease in their hydrogen flow rates/fluxes: e.g. on a 12.5 μm palladium silver membrane the relative hydrogen flux decreased 7.5% for 1 vol.% of CO at 350 °C and 21.9 % for 5 vol.% of CO. The temperature dependence can be explained by a shift in the CO adsorption equilibrium towards a higher value, relative to hydrogen, for lower temperatures. For this reason, in this experimental study, at 500 °C no competitive adsorption of CO is considered and the only reason for a decrease in hydrogen flow rate is due to the inserted inert. These results are then compared to the ones obtained at 350 °C: by doing so it is possible to verify if at lower temperatures CO inhibits the palladium alloy membrane.

Table 12 – Experimental values for relative hydrogen flow rate at 500 °C and 350 °C.

<table>
<thead>
<tr>
<th>CO feed concentration [vol.%]</th>
<th>Relative H₂ flow rate 500 °C</th>
<th>Relative H₂ flow rate 350 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.75</td>
<td>0.84</td>
<td>0.82</td>
</tr>
<tr>
<td>1.5</td>
<td>0.655</td>
<td>0.645</td>
</tr>
<tr>
<td>2.25</td>
<td>0.5</td>
<td>0.49</td>
</tr>
<tr>
<td>3</td>
<td>0.325</td>
<td>0.345</td>
</tr>
</tbody>
</table>
Figure 6.1 – Relative hydrogen flow rate as a function of the CO feed concentration. Feed pressure = 0.2 MPa; Permeate pressure = 0.15 MPa.

The two trends, at 500 °C and 350 °C, are very similar, which means that there is no inhibition due to competitive adsorption of CO. The only reason for which there is a decrease in the relative hydrogen flux is due to the dilution effects of helium in the feed. This result is different than Peters et al. (2007), Mejdell et al. (2009), and Kurokawa et al. (2014) because in this experimental study a thicker membrane is evaluated and it seems that with these experimental conditions no inhibition due to CO is present.
7 Conclusions

7.1 Summary and Conclusions

The effect of competitive adsorption of steam, carbon monoxide, methane, and nitrogen through a thin Pd-Ag membrane has been investigated. Comparisons were made between the experimental and predicted hydrogen permeation rates without accounting for mass transfer limitations because of the design of the separator apparatus. The gas mixtures could have decreased the hydrogen flux by adsorbing on the palladium membrane and, consequently, lower the quantity of active sites for hydrogen dissociation. However, all additives have no or very little inhibition effects on hydrogen permeation between 350 °C and 500 °C and this is due probably to the thickness of the membrane and high temperatures.

The demand for hydrogen production technology for smaller scale is growing driven by the development of fuel cell technology on one hand and the distributed nature of renewable sources (biomass/biogas) on the other hand. Hydrogen vehicle filling stations, electricity distribution sub-station, distributed ammonia production, low emission auxiliary power units running on diesel, and computers and mobile phones running on methanol are examples of the wide range of scale. Reduced cost of reforming technology through innovation and technological progress, such as palladium membranes, are needed to avoid that the hydrogen produced becomes prohibitively expensive.

Further investigations on palladium silver membranes are recommended because it is imperative to understand the optimal thickness of the palladium layer. As mentioned before, higher the thickness of the membrane, lower is the flux of hydrogen and higher is the cost. However, with lower thicknesses there are two major problems: (i) the membrane can break; (ii) competitive adsorption. For this reason this experimental study suggests further investigations to understand the minimum thickness, where at high temperatures there is no competitive adsorption and no mechanical problems.
8 References


Cheng Y. S. "Membrane and membrane reactor design for hydrogen production", Hong Kong University of Science and Technology, (2001).


