

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**HYDROGEN PRODUCTION FROM BIOGAS IN A
MEMBRANE REACTOR**

by

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October, 2022

İZMİR

HYDROGEN PRODUCTION FROM BIOGAS IN A MEMBRANE REACTOR

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**by
Yağmur NALBANT ATAĞ**

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İZMİR

Ph.D. THESIS EXAMINATION RESULT FORM

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HYDROGEN PRODUCTION FROM BIOGAS IN A MEMBRANE REACTOR

ABSTRACT

The interest in the production of clean hydrogen has increased due to the depletion of fossil fuels and the increase in energy demand. The hydrogen production by the membrane reactors that provide both hydrogen production and hydrogen separation in the same device is increasing day by day. In this thesis, the mathematical modeling method is used to improve the performance of the membrane reactor providing hydrogen production from biogas and methane. 1-dimensional models of a membrane reactor were developed by MATLAB program and validated separately. The temperature distributions of the reactor, the change of molar flow rates of all species, methane conversion, and hydrogen recovery were investigated along the reactor length. The validated 1-dimensional membrane reactor model was integrated into an integrated system consisting of CO₂ capture system and various plant components and the system-level model was developed in the MATLAB program using principles of electrochemistry (reaction kinetics) and thermodynamics (energy and exergy analysis). The effects of some operating parameters (operating temperature, steam-carbon ratio, and reaction pressure) on system performance were investigated. Then, the exergy destruction rates of each component in the integrated system and the exergy destruction rate values of each component were examined. Moreover, in order to better understand the operating principle of the membrane reactors, the experimental studies were realized at the Membrane Technology Institute in Italy. Finally, 2-dimensional membrane reactor models were developed using COMSOL Multiphysics software to investigate the behavior of the reactor through both the axial and radial directions.

Keywords: Membrane reactor, hydrogen production, mathematical model, CO₂ capture, energy, exergy

MEMBRAN REAKTÖRDE BİYOGAZDAN HİDROJEN ÜRETİMİ

ÖZ

Fosil yakıtların tükenmesi ve enerji talebindeki artış nedeniyle temiz hidrojen üretimine ilgi artmıştır. Aynı cihazda hem hidrojen üretimi hem de hidrojen ayrımı sağlayan membran reaktörlerde hidrojen üretimi her geçen gün artmaktadır. Bu tezde, besleme gazından (biyogaz ve metan) hidrojen üretimi sağlayan membran reaktörün performansını iyileştirmek için matematiksel modelleme yöntemi kullanılmıştır. MATLAB programı kullanılarak, bir membran reaktörün 1- boyutlu modelleri geliştirilmiş ve ayrı ayrı doğrulanmıştır. Reaktörün sıcaklık dağılımları, tüm türlerin molar akış hızlarının değişimi, metan dönüşümü ve hidrojen geri kazanımı reaktör uzunluğu boyunca incelenmiştir. Doğrulan 1-boyutlu membran reaktör modeli, CO₂ yakalama sistemi ve çeşitli tesis bileşenlerinden oluşan entegre bir sisteme entegre edilmiş ve MATLAB programı ile elektrokimya (reaksiyon kinetiği) ve termodinamik (enerji ve ekserji analizi) ilkelerini kullanarak sistem düzeyinde model geliştirilmiştir. Bazı çalışma parametrelerinin (çalışma sıcaklığı, buhar-karbon oranı ve reaksiyon basıncı) sistem performansı üzerindeki etkileri araştırılmıştır. Daha sonra entegre sistemdeki her bir bileşenin ekserji yıkım oranları ve her bir bileşenin ekserji yıkım hızı değerleri incelenmiştir. Dahası membran reaktörlerin çalışma prensibini daha iyi anlamak için, deneysel çalışmalar İtalya'daki Membran Teknoloji Enstitüsü'nde gerçekleştirilmiştir. Son olarak, reaktörün davranışını hem eksenel hem de radyal yönlerde araştırmak için COMSOL Multiphysics yazılımı kullanılarak 2-boyutlu membran reaktör modelleri geliştirilmiştir.

Anahtar kelimeler: Membran reaktör, hidrojen üretimi, matematiksel model, CO₂ yakalama, enerji, ekserji

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LIST OF SYMBOLS

A_c	Cross sectional area of the reactor, m ²
Bi	Dimensionless quantity used in heat transfer calculations - Biot number, -
B_{H_2}	Hydrogen permeability, mol/(s·m ² ·Pa ⁿ)
B_0	Geometrical factor, m ²
c_p	Specific heat capacity, J/(kg·K)
C	Concentration, mol/m ³
$Conv_{sys_CH_4}$	Methane conversion in the system
d_{pore}	Pore diameter, m
D_{ax}	Axial dispersion coefficient, m ² /s
$D_{i,j}$	Binary diffusion coefficient, m ² /s
DEN	Adsorption of reacting species to active catalyst domains, -
D_H^0	Pre-exponential factor of the atomic hydrogen diffusion coefficient, m ² /s
$\overline{ex}_i$	Exergy rate of i stream, kJ/kmol
E_i	Activation energy, kJ/kmol
$\dot{Ex}$	Exergy rate, W
$\dot{Ex}_D$	Exergy destruction rate, W
f	Local frictional pressure drop
$\vec{f}$	Force source term, N/m ³
$\vec{f}_1$	Viscous resistance factor, Pa·s/m ²
$\vec{f}_2$	Inertial resistance factor, Pa·s ² /m ³
F	Molar flow rate, kmol/h
g	Gravitational acceleration, m/s ²
G	Mass specific gas flow rate, kg/(m ² ·h)
$\Delta \bar{h}_i$	Adsorption specific enthalpy, kJ/kmol
h	Coefficient of external mass transfer, kmol/(m·h)
$\bar{h}_i$	Specific enthalpy, kJ/kmol

$\tilde{h}^0$	Molar enthalpy of formation, kJ/kmol
$\overline{HHV}$	Higher heating value, J/mol
J_{H_2}	Hydrogen permeation flux, kJ/(m ² ·h)
k_i	Reaction rate constant, kmol·bar ^{0.5} /(kg _{cat} ·h)
$k_{0,i}$	Pre-exponential factor for i th reaction, kmol·bar ^{0.5} /(kg _{cat} ·h)
k_{Des}^0	Pre-exponential factor of the desorption kinetic constant, m ² /mol·s
K_j	Adsorption constant of species j, bar ⁻¹
$K_{j,0}$	Pre-exponential factor for adsorption constant, bar ⁻¹
K_{eq}	Equilibrium constant, bar ²
$\overline{LHV}$	Lower heating value, J/mol
$\dot{m}$	Mass flux, kg/(m ² ·s)
M or MW	Molecular weight, kg/kmol
$\dot{n}$	Molar flow rate, mol/s
n_{CH_4}	Mol number of methane, mol
N_b	Total bulk concentration of free sites, mol _{pd} /m ³
N_s	Total superficial concentration of free sites, mol _{pd} /m ²
ΔP_j	Linear driving pressure, kPa
P_j	Partial pressure of species j, kPa
$P_{j,eq}$	Equilibrium partial pressure of species j, kPa
P_m	Perimeter of membrane, m
Pr	Prandtl number, -
$\dot{q}$	Heat flux, W/m ²
$\dot{Q}$	Heat transfer rate, W
r	Radius, m
r_i	Reaction rate of i th reaction, kmol/(kg _{cat} ·h)
r_f	Rate of forward turnover, s ⁻¹
$\bar{R}$	Universal gas constant, kJ/kmol·K
Re	Dimensionless quantity for determining the flow pattern type, Reynolds number, -
$Recovery_{H_2}$	Hydrogen recovery

$\bar{s}$	Specific entropy, J/(mol·K)
S_m	Hydrogen permeation area per unit volume of sweep gas channel, m ² /m ³
S_0	Sticking coefficient for a Pd-based clean surface, -
t	Time, s
T	Temperature, K
T_{ref}	Reference temperature, K
u	Velocity, m/s
U	Overall heat transfer coefficient, W/(m ² ·K)
v	Superficial velocity, m/s
$\dot{W}$	Power, W
m_{cat}	Mass of catalyst, kg
x	Molar fraction, -
X_{CH_4}	Methane conversion
$Yield_{CO_2}$	Carbon dioxide yield
$Yield_{H_2}$	Hydrogen yield
y_D	The ratio between the exergy destruction rate of a component and the exergy rate of the fuel
z	Length of the reactor, m

List of Greek Letters

α	Adsorption term in the power law
β	Contribution
δ	Thickness, m
ε	Porosity, -
η	Equilibrium parameter
$\eta_{th,HHV}$	Thermal HHV efficiency
$\eta_{th,LHV}$	Thermal LHV efficiency
θ	Surface coverage due to atomic hydrogen, mol _H /mol _{Pd}
λ_{er}	Effective radial thermal conductivity of the bed, kJ/(m·h·K)
$\lambda_{j,0}$	Jump frequency, s ⁻¹

μ	Dynamic viscosity, Pa·s
$\nu_{i,j}$	Stoichiometric coefficient, -
ξ	Atomic hydrogen concentration in Pd bulk, mol _H /mol _{Pd}
π	Hydrogen permeance, mol/(s·m ² ·Pa ⁿ)
ρ_b	Density, kg/m ³
σ	Hydrostatic pressure in the metal lattice, Pa
τ	Tortuosity, -
$\bar{\bar{\tau}}$	Stress tensor, Pa
Φ	Temperature variation, K
ψ	Heat generated by chemical reaction, W/m ³
Ω	Collisional integrals

List of Subscripts and Superscripts

Ads	Adsorption
amb	Ambient
an	Annulus
BS	Bulk-to-surface
cv	Control volume
CH	Chemical
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
comp	Compressor
Des	Desorption
Diff	Diffusion
e	Exit
ex	Exergy
f	fluid
H ₂	Hydrogen
H ₂ O	Water
HEX	Heat exchanger

i	Inlet
i	Number of reaction
j	Species
min	Minimum
O ₂	Oxygen
0	Reference value
perm	Permeation
PH	Physical
r	Reformer
react	Reaction
rest	Residual
s	Solid
SB	Surface-to-bulk
ret	Retentate
sep	Separation
sys	System
SMR	Steam methane reforming
S/C	Steam to carbon ratio
Tot	Total
Vs	Viscous
*	Partial

ABBREVIATIONS

BFM	: Binary friction model
CR	: Conventional reactor
DSR	: Direct steam reforming
HH	: Hou and Hughes
HHV	: Higher Heating Value
H ₂ O	: Water
H ₂ S	: Hydrogen sulfide
LHV	: Lower Heating Value
MR	: Membrane reactor
NH ₃	: Ammonia
NK	: Numaguchi and Kikuchi
Pd	: Palladium
Rxn	: Reaction
SR	: Steam reforming
XF	: Xu and Froment
WI	: Wei and Iglesia
WGS	: Water gas shift

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The increase in global energy demand and environmental problems, such as the depletion of fossil fuels, air pollution, and global warming, have promoted the interest in the efficient and clean utilization of energy resources and carriers. In this regard, many efforts have been put on hydrogen generation as a clean fuel due to its high gravimetric energy density and low environmental impact (e.g., when used in fuel cells). Hydrogen can be produced by different methods such as thermochemical (e.g., reforming and gasification), electrolytic (e.g., electrolysis), photonic (e.g., photoelectrochemical and photobiological), and biological (e.g., microbial biomass conversion and photobiological) processes (Acar and Dincer, 2020; Dawood et al., 2020; Iulianelli and Basile, 2020a).

Currently, the most commonly used hydrogen production method in industrial applications is the steam reforming process from natural gas (Adolf et al., 2017). Conventionally, hydrogen is produced using this process by a series of chemical reactors including a steam reformer and two-stage water-gas shift reactors (high and low temperatures), and hydrogen purification units. Although these conventional reactors (CRs) are widely used in industrial applications, they have some significant disadvantages such as their thermodynamic equilibrium limitation, internal diffusion resistance, carbon formation, and cost of material resistance to high temperature. In addition, the required high amount of heat input for the chemical reactions is usually provided by a furnace that burns fuels, causing environmental pollution (Lu and Xie, 2016). To overcome these disadvantages, other types of reactors have been developed. Among these reactors, membrane reactors (MRs) allow the hydrogen production and purification in the same device at operating temperatures between 673 K and 923 K (Kim et al., 2018; Amiri et al., 2020). Compared to the CR, Pd-based MRs do not need an additional purification unit, and thus the hydrogen is easily produced with a lower energy requirement (Amiri et al., 2020). In the aforementioned MRs, hydrogen

produced in the reaction side constantly permeates through the Pd/Pd-alloy membrane, and thus the steam reforming reactions are always in the forward direction, and this eliminates the thermodynamic equilibrium limitation problem. In addition, depending on the MR type, parameters such as the size of the catalyst particle, the capacity of heat transfer, the membrane cost, and the performance can be improved to make them advantageous compared to the CRs (Lu and Xie, 2016).

In this thesis, the mathematical modeling method is used to improve the performance of the membrane reactor providing hydrogen production from biogas. Using the MATLAB program, 1-D models of a membrane reactor were created according to two different case study analyses and validated separately with the results of two reference studies in the literature. According to the first case study analysis, the temperature distributions for both the permeation and the reaction sides of the reactor were investigated with the developed 1-D membrane reactor model. In addition, the changes in molar flow rates of all species, methane conversion, and hydrogen recovery along the reactor length were investigated. According to the second case study analysis, the temperature distributions for both the permeation and the reaction sides of the reactor were investigated similarly using the developed 1-D membrane reactor model. In addition, parametric analysis of operating temperature, reaction pressure, and steam to carbon ratio parameters on methane conversion and hydrogen recovery were realized. The 1-D membrane reactor model developed in the first case study was integrated into an integrated system consisting of CO₂ capture and various plant components (compressor, boiler, burner, pump, blower, and two mixers) and the system-level model was developed in the MATLAB program, using principles of electrochemistry (reaction kinetics) and thermodynamics (energy and exergy analysis). The changes in the molar flow rates of each species and the temperature along the reactor length were investigated. The effects of some operating parameters (operating temperature, steam-carbon ratio, and reaction pressure) on system performance (methane conversion, hydrogen yield, CO₂ efficiency, and thermal efficiency (based on LHV and HHV)) were investigated. In addition, the exergy destruction rates of each component in the integrated system and the exergy destruction rate (W) values of each component according to the change of these

parameters were examined. Moreover, in order to validate the developed mathematical models, an experimental setup that enables the production of hydrogen from biogas with a membrane reactor was set up and the experimental studies were realized at the Membrane Technology Institute in Italy. However, due to the technical problems experienced there, only calibration and permeability tests of the Pd/Al₂O₃ membrane separator module were carried out. Finally, 2-D membrane reactor models were developed using COMSOL Multiphysics software to investigate the behavior of the reactor through both the axial and radial directions. In 2-D models, four physics (transport concentrated species, Darcy's law, heat transfer in fluid, and chemistry) were used to define mass, energy, and reaction kinetics values.

1.2 Motivation

This thesis focuses on the mathematical modeling of a membrane reactor at single and integrated system levels. The main motivations of this thesis are as follows;

- 1-D and 2-D modeling approaches have been shown to be powerful tools for membrane reactor modeling. Although there are few 2-D mathematical models of membrane reactors in the literature, no study has been conducted on the detailed modeling of membrane reactors that produce hydrogen from biogas with the four different physics used to investigate the changes of mass, energy, and momentum.
- To the author's knowledge, no study has been found in the literature on performing both energy and exergy analysis of an integrated system consisting of a membrane reactor and a CO₂ capture system.

1.3 Objectives

The main aim of this thesis is to develop a one-dimensional model and two-dimensional models of the membrane reactor producing hydrogen from biogas or methane and investigate the effects of some operating parameters on the performance of the membrane reactor, and then, combine it with an integrated system consisting of a membrane reactor and CO₂ capture system. Using this system level model, energy and exergy analyses of an integrated system (including a membrane reactor, CO₂

capture system, and the other components) that converts methane into hydrogen and carbon dioxide for the different energy technologies (e.g. fuel cells or power-to-gas) is performed. The objectives of the thesis are listed below;

- To develop a 1-D membrane reactor model to investigate the changes in the molar flow rates of each species, the temperatures in the reaction and permeation sides, and membrane reactor performances (methane conversion and hydrogen recovery).
- To develop a mathematical model of an integrated system including a membrane reactor, CO₂ capture system, burner, boiler, heat exchanger, compressor, mixers, and pump, and examine the effects of some operating parameters (operating temperature, reaction pressure, and steam-to-carbon ratio) on system performance (methane conversion, hydrogen yield, CO₂ efficiency, and thermal efficiency (based on lower heating value and higher heating value)).
- To set an experimental setup that enables the production of hydrogen from biogas with a membrane reactor at the Membrane Technology Institute in Italy and to realize the experimental studies in order to better understand the operating principle of the membrane reactors.
- To develop a 2-D membrane reactor model in order to investigate the distributions of temperatures and molar concentrations along both the axial and radial directions.

1.4 Thesis Outline

The second chapter is devoted to the introduction of membrane reactor technologies. A comprehensive review of the mathematical modeling studies on the MRs for hydrogen production from methane was conducted covering all main aspects of modeling. Recent papers on this topic were investigated, compared, and discussed. The different reaction kinetic expressions for steam-methane reforming reactions were investigated, and the reaction kinetics coefficients used in different modeling studies in the literature were listed. In addition, the modeling equations of each step of the hydrogen permeation process were investigated in detail, and the comparison of different modeling studies on hydrogen permeation through membranes found in the literature was proposed. Finally, the different modeling approaches for the MRs were

investigated based on the phases involved (pseudo-homogeneous and heterogeneous) and spatial dimensions (one, two, and three-dimensional).

The third chapter covers the information on the materials used in the experiments, the experimental steps, and the procedure followed in the performance tests, in detail.

The fourth chapter includes mathematical modeling of the membrane reactor in single and integrated system levels. Firstly, the 1-D modeling of MR is explained and the modeling equations are given in detail. Secondly, a mathematical model for an integrated system is presented. Moreover, a thermodynamic model for the integrated system (including an MR, CO₂ capture system, boiler, burner, pump, compressor, mixers, and heat exchanger) is studied, and the detailed equations used in the energy and exergy analyses are given.

In the fifth chapter, the results of the 1-D model of the membrane reactor according to Case Study-1 and Case Study-2, the mathematical model of the integrated system, and the 2-D models of the membrane reactor are given and discussed in detail.

The sixth chapter gives conclusions related to the studies in this thesis.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1 Membrane Reactors

Membrane reactors used for hydrogen production consist of two sides, which are the reaction side (the zone where feed stream flows) and the permeation side (the zone where hydrogen permeated through the membrane). The schematic of a dense membrane-based MR showing its main components and the operation principle are shown in Figure 2.1. These reactors also enable hydrogen production with lower external energy input (Amiri et al., 2020). In addition, as hydrogen is continuously removed from the reaction side to the permeation side, membrane reactors are not bound to the thermodynamic limitations of chemical equilibrium (Barelli et al, 2008; Bruni et al., 2019).

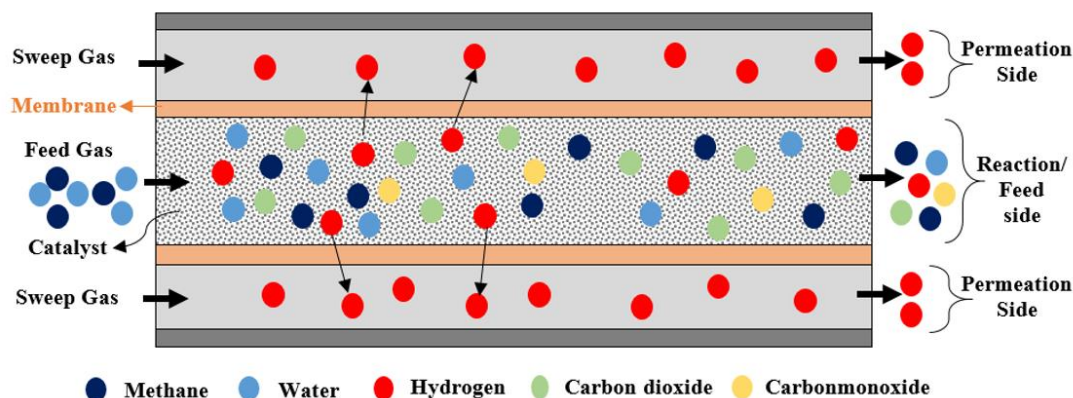


Figure 2.1 Schematic diagram of dense membrane based a membrane reactor for hydrogen production from a gas mixture showing its main components and operation principle

2.1.1 Membrane Type

Membranes used in membrane reactors are basically barriers that do not allow some components in a feed gas mixture to permeate. The performance of membrane reactors mostly depends on the properties of the membrane (e.g., permeability, porosity, thickness, and geometry). The choice of membrane-type mostly depends on some parameters such as the selectivity of separation, productivity, life-time, mechanical

and chemical stabilities at the operating conditions, and cost (Iulianelli and Basile, 2019; Gallucci et al., 2011). Membranes can be classified according to their nature, geometry, and separation regime (Gallucci et al., 2011), as shown in Figure 2.2.

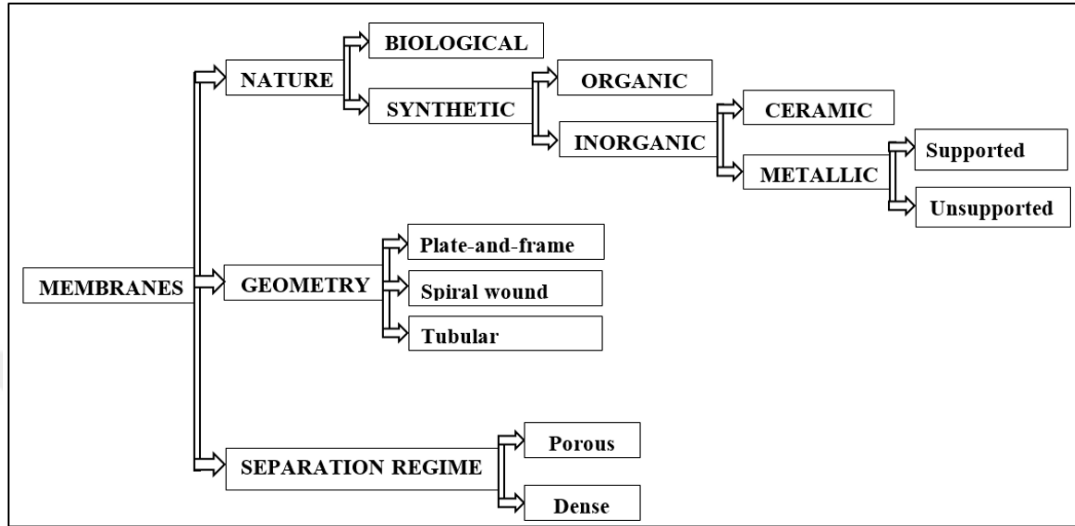


Figure 2.2 Classification of membrane types (based on Ref. (Gallucci et al., 2011))

2.1.1.1 Membrane Nature

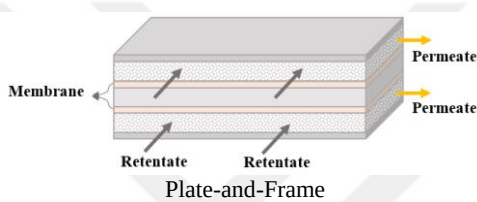
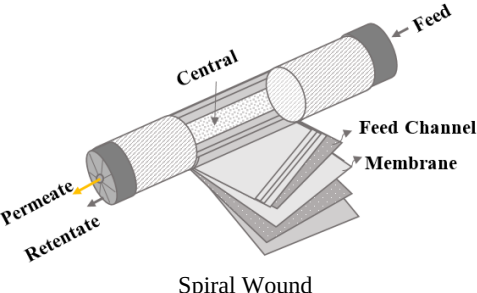
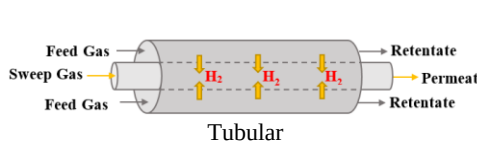
Membranes can be classified according to their nature as biological and synthetic membranes. Biological membranes have some limitations such as pH and operating temperature ($<100^{\circ}\text{C}$), and some disadvantages such as the sensitivity to microbial attack (Gallucci et al., 2011; Xia et al., 2003). Synthetic membranes can be subdivided into two groups: organic membranes operating between $100\text{--}300^{\circ}\text{C}$ and inorganic membranes operating above 250°C (Gallucci et al., 2011). Organic membranes are made of natural (e.g., rubber, wool, and cellulose) or synthetic (e.g., polystyrene, polyamide, and polytetrafluoroethylene) polymers. Inorganic membranes consist of different materials such as metal, carbon, ceramic, zeolite, silica, and oxides. When the inorganic membranes are compared to the organic membranes, they have some advantages such as resistance to harsh environments (e.g., chemical degradation and pH), resistance to high pressure drops, easy cleanability after fouling, and easy catalytic activation despite their high capital cost (Iulianelli and Basile, 2019; Gallucci et al., 2011). The most important advantage of the inorganic membranes is the long-term stability at high temperatures ($300\text{--}800^{\circ}\text{C}$), even in some cases the ceramic

membranes can be used over 1000°C (Gallucci et al., 2011; Smart et al., 2013). Metallic membranes used for hydrogen separation/purification (e.g., Pd or Pd alloys such as Pd-Ag, Pd-Au, Pd-Cu etc.) can be mainly split into two groups: unsupported membranes (or self-supported) and supported (or composite) membranes. Self-supported Pd membranes are generally constituted of thicker layers ($> 50 \mu\text{m}$) to ensure a certain mechanical resistance. Therewithal, they possess full hydrogen permselectivity; however, due to the larger thickness they show poor hydrogen permeability and they are less economically viable for practical applications due to the high cost of Pd. In particular, to reduce the cost of the membrane and enhance the hydrogen permeability, the interest in the supported or composite membranes is increasing day by day although they may show finite hydrogen permselectivity (thinner Pd-layers may involve presence of pin-holes) (Li et al., 2015). Since Pd-based composite or supported membranes can be produced as a thin metallic layer deposited onto porous substrates, they have thinner Pd thickness, high mechanical resistance ensured by the porous support, and high hydrogen permeability, and thus more economical advantage (Liguori et al., 2014). Liguori et al. (2014) investigated two different Pd-based composite membranes with porous stainless steel (PSS) and ceramic substrates. Firstly, this study showed that the PSS substrate has good weldability, high mechanical resistance, and a more suitable thermal expansion coefficient than the ceramic substrate (because much closer to the separative metallic layer). However, it was also found that this substrate has some manufacturing problems due to its high rough surface and large pore size. In addition, due to the absence of an intermetallic layer, the intermetallic diffusion problem exists particularly in the case of PSS substrate utilization, since the Pd-layer is directly in contact with this porous substrate. Secondly, this study showed that ceramic substrates, which are chemically inert and stable for a wide range of temperatures, provide the manufacture of defect-free membranes. However, it is found that the cost of the membranes using this substrate is relatively high due to plenty of coating and sintering processes.

2.1.1.2 Membrane Housing

Protection and stability of membrane against operating conditions such as pressure are provided by the membrane housing (Gallucci et al., 2011). Membranes can be classified into three groups according to membrane housing/geometry: plate-and-frame, spiral wound, and tubular. Table 2.1 shows a comparison of three different membrane housing modules according to their advantages and disadvantages.

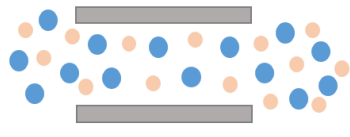
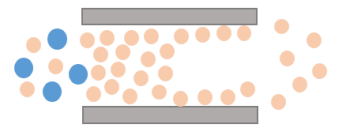
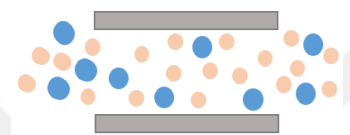
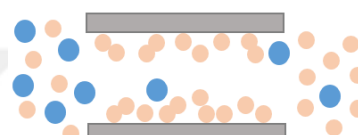
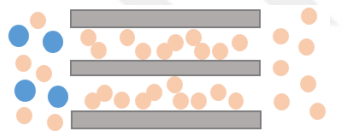
Table 2.1 Comparison of three different membrane housing modules according to their advantages and disadvantages (Adapted from Gallucci et al. (2011))

Membrane Module	Advantages	Disadvantages
 Plate-and-Frame	- Reasonable ratio between the membrane surface and volume - Well-developed equipment - Easy membrane modification	- Difficulty with cleaning - Expensive - Sensitive to plugging at flow stagnation points
 Spiral Wound	- Compact - High ratio of membrane surface area to volume - Low cost - Minimum energy consumption	- Difficulty with cleaning - Not appropriate for very viscous fluids - If the membrane is degraded, the whole module will be changed.
 Tubular	- Easy cleaning - Good control for hydrodynamic control - Each tube can be replaced independently of the whole module.	- Relatively high volume necessary for unit membrane area - High energy consumption - Relatively high cost

2.1.1.3 Membrane Separation Regime

Membranes can be categorized according to the membrane separation regimes as porous and dense membranes. In the porous membranes, different mechanisms such as viscous diffusion, Knudsen diffusion, surface diffusion, capillary condensation, multi-layer diffusion, and molecular sieving occur (Gallucci et al., 2011). Table 2.2 shows the schematic of different mechanisms used in the porous membranes and their important features.

Table 2.2 Schematic of different mechanisms used in the porous membranes and their features (Adapted from Gallucci et al. (2011))

 Viscous Mechanism $d_{ave,pore} > d_{ave,free-path}$ - No separation takes place.	 Knudsen Mechanism $d_{ave,pore} \cong d_{ave,free-path}$ - Gas molecules collide with the wall of solid pores rather than each other. - Gas permeability resistance depends on the collision between the molecule and the pore wall. $\frac{G}{\sqrt{2M_iRT}}$
 Surface Diffusion - One of the permeating molecules is absorbed on the pore wall. - This can decrease the effective pore dimensions that inhibit the molecular transfer of species.	 Capillary Condensation - One of the molecules condenses within the pores because of capillary forces. - The transfer of large molecules is easy with the capillary condensation.
 Multi-layer Diffusion - If the interactions between molecule and surface are strong, multi-layer diffusion occurs. - It is an intermediate mechanism between capillary condensation and surface diffusion.	 Molecular Sieving $d_{ave,pore} \ll d_{ave,free-path}$ It only allows the permeation of the smaller molecules.

In order to obtain high purity hydrogen permeation streams, dense metal membranes are generally preferred. However, the most preferred material used for hydrogen perm-selective membranes fabrication is Pd or Pd alloys, which are one of the face-centered cubic (FCC) metals (Arratibel Plazaola et al., 2017). Years ago, it was investigated and found that the body-centered cubic (BCC) metals have a high hydrogen diffusion rate and low thermal expansion for hydrogen purification. Elements found in Group 5 at the Periodic Table such as V, Nb, and Ta have higher permeation rates than FCC metals and their alloys (Arratibel Plazaola et al., 2017).

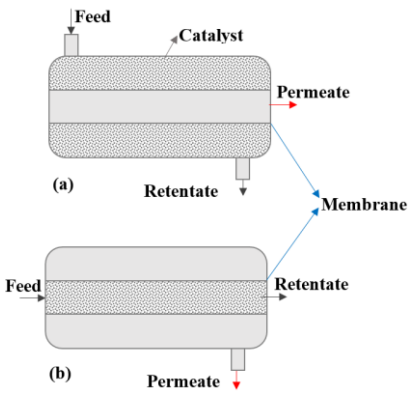
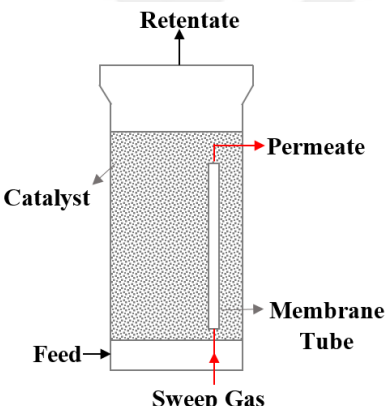
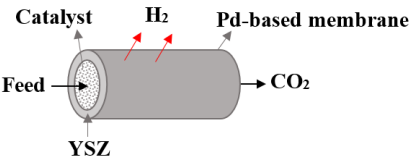
However, their surface is easily oxidized with the presence of oxygen even at low temperatures (~ 100 °C) (Paglieri and Way, 2002). This problem can be solved by covering their surface with another material, generally chosen as Pd. Another problem for BCC metals is the embrittlement phenomenon and it is not solved yet and constitutes the most crucial issue for the adoption of metals such as Ta, V, and Nb for membrane fabrication and utilization, even though they show the highest hydrogen permeabilities compared to the other metals (Arratibel Plazaola et al., 2017). Therefore, apart from the aforementioned metals, Pd-based alloys are the most preferred materials due to their high solubility and superior hydrogen permeability (Gallucci et al., 2011).

In the dense Pd-based membranes, the transport of molecules occurs through the solution-diffusion mechanism that consists of seven steps. A detailed explanation of hydrogen transport mechanisms can be found in the Section 2.6.

2.1.2 Membrane Reactor Configurations

In the literature, different membrane reactor configurations are found. These configurations are packed bed membrane reactor (PBMR), fluidized bed membrane reactors (FBMRs), and micro-membrane reactors (MMRs). PBMR is the most studied configuration due to its advantages in particular related to the integration of membrane and simplicity in operation (Gallucci et al., 2017). Table 2.3 shows the schematic and properties of these different membrane reactor configurations.

Table 2.3 Schematic and properties of different membrane reactor configurations

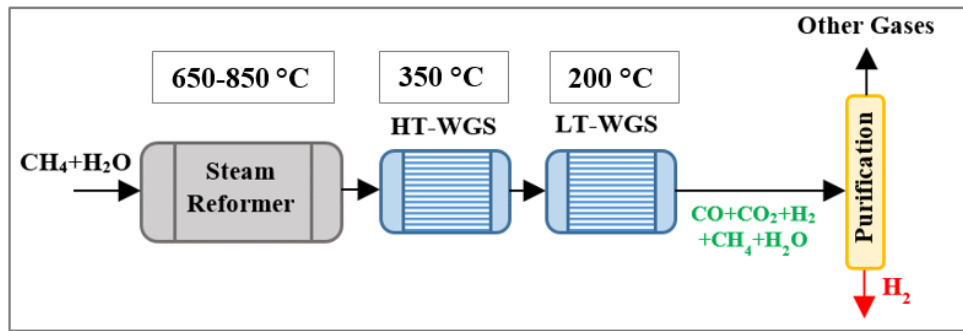
Membrane Reactor Configuration	Main features
 Packed bed membrane reactor: (a) tube and (b) shell catalyst configuration	- Membrane behaves as an extractor or a distributor (Rahimpour et al., 2017). - The following reactions may occur: Reforming of methane and alcohols, autothermal reforming, and partial oxidation reforming (Rahimpour et al., 2017). - Catalyst is located inside the reactor in the fixed bed configuration and in contact with the membrane (Gallucci et al., 2017). - This configuration allows the usage of sweep gas on the permeation side in order to provide the driving force for gas separation (Gallucci et al., 2017). - The main disadvantages are high-pressure drop, mass transfer limitations because of large particle size, the complexity of reaction heat for supplied and extraction (Rahimpour et al., 2017).
 Fluidized bed membrane reactor	- This configuration includes one membrane or a membrane stack located in the catalytic bed with bubbling or turbulent conditions (Rahimpour et al., 2017). - The following reactions may occur: autothermal reforming of methane, the synthesis of methanol (Rahimpour et al., 2017). - The main advantages are negligible pressure drop and mass transfer limitations due to the small particle size of catalyst, ability to work in isothermal conditions, easiness in the arrangement of membrane bundles, etc. (Gallucci et al., 2017; Rahimpour et al., 2017). - The main disadvantages are the sealing of the membrane, the erosion of the inside of the reactor, and the abrasion of the catalyst (Gallucci et al., 2017; Rahimpour et al., 2017).
 Hollow-fiber micro-membrane reactors	- Typical sizes of 1–1000 μm. - Three possible configurations: planar, hollow-fiber, and monolithic. - The main advantages are the better mass/heat transfer due to decrease in the length scale, the enhancement of the ratio of area to volume due to very high intensification (Rahimpour et al., 2017).

2.2 Comparison of Membrane Reactor and Conventional Reactor

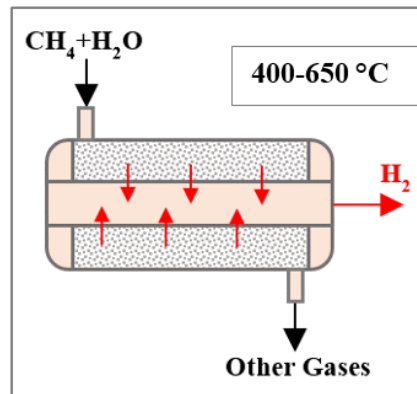
Today, most of the hydrogen is produced from natural gas by the steam reforming (SR) process (Iulianelli et al., 2016c). More precisely, hydrogen is produced by the conventional reactors consisting of a steam reformer and two-stage water-gas shift reactors (high and low temperatures), and a purification unit (pressure swing adsorption, membrane technologies, and cryogenic distillation (Iulianelli and Basile 2019). Although conventional reactors are widely used in industrial applications, they have some significant disadvantages as follows (Amiri et al., 2020):

- The restriction of thermodynamically chemical equilibrium,
- Internal diffusion resistance,
- The formation of carbon,
- The catalyst deactivation,
- Material problem due to high temperature,
- Environmental emissions due to providing the required heat for chemical reactions.

In order to overcome the disadvantages of conventional reactors, membrane reactors, which enable simultaneous production and separation or purification of hydrogen, can be used. These reactors have a compact structure since both chemical reactions and separation/purification processes take place in the same process unit. Therefore, compared to conventional reactors, membrane reactors provide hydrogen production with lower energy requirements and easier management of operation (Figure 2.3) (Amiri et al., 2020).



(a) Conventional Reactor



(b) Membrane Reactor

Figure 2.3 Comparison of conventional and membrane reactors

The main advantages of membrane reactor are given as follows:

- Since hydrogen produced by chemical reactions in the membrane reactor is continuously removed from the reaction side through the membrane, and these reactions are completely forward, the thermodynamic chemical equilibrium limitation is eliminated, meanwhile intensifying the whole process.
- It is possible to use materials at lower temperatures, favoring globally the energy saving.
- Some problems inside the reactor such as the heat transfer capacity, the overheating catalyst, high-pressure drops, the cost, and the performance can be improved depending on the membrane reactor type.

2.3 Hydrogen Production Using Membrane Reactors through the Utilization of Renewable Resources

Hydrogen production from fossil fuels is not considered as a sustainable option due to the depletion of fossil fuels and the environmental effects, such as greenhouse gas, acid rains, and global warming, that they cause upon their utilization to generate useful energy forms. Thus, hydrogen should be produced through renewable resources through environmentally-friendly methods and technologies. Electrolysis of water, which is one of these technologies, can be used to produce hydrogen using electricity produced from different renewable energy sources such as solar, wind, hydro, biomass, and geothermal. However, this technology is still under development and costly. On the other hand, hydrogen production by chemical reforming processes of various hydrocarbons is more preferable currently (Minh et al., 2018; Gao et al., 2018). However, in order to reduce the utilization of fossil fuels and its associated environmental problems, interest in hydrogen production from ethanol, methanol, glycerol, and ammonia, and biofuels produced from biomass is increasing (Palma et al., 2020). Moreover, the use of biomass can prevent carbon dioxide from reaching atmospheric levels due to the re-growth cycle of trees and plants, in addition, this can also reduce the methane amount that is emitted from the organic matter deterioration (Gallucci et al., 2011).

Currently, the interest in hydrogen production from liquid or gas biomass-derived fuels produced by thermochemical, biological, and transesterification processes is increasing due to both easy transportation and pre-prepared available substructures (Xuan et al., 2009). Some examples of these fuels are bioethanol by gasification process, biogas by anaerobic digestion process, bioethanol by alcoholic process, and biodiesel and bio glycerol by transesterification. Figure 2.4 shows the hydrogen production methods from different biomass sources. Among thermochemical methods, gasification of biomass is generally preferred to produce a hydrogen-rich syngas. Among biological methods, anaerobic digestion is a mature process that involves the production of biogas through the degradation of organic materials (Chen et al., 2008).

Biogas should go through a thermochemical conversion (e.g. reforming) to produce hydrogen.

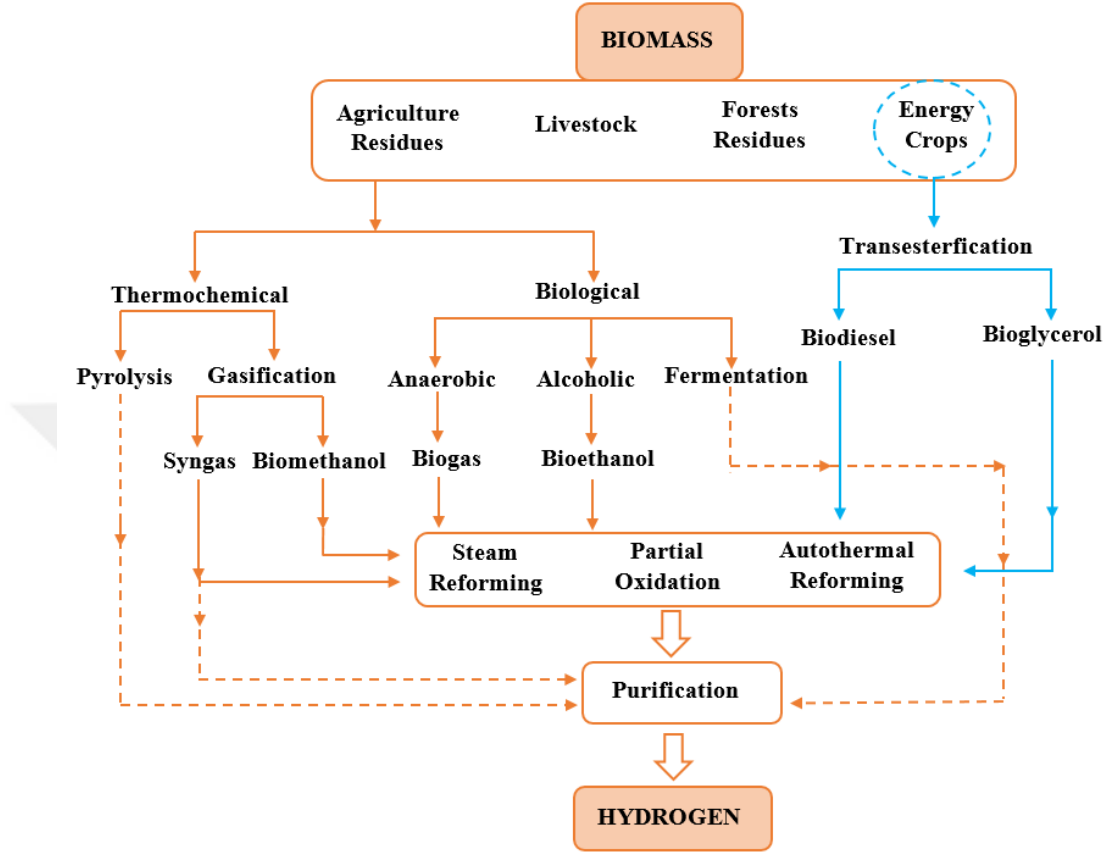
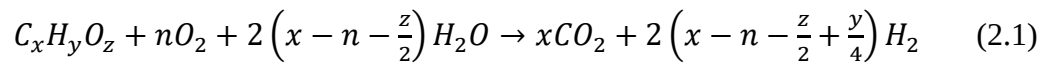


Figure 2.4 Hydrogen production methods from different biomass sources (Modified from Xuan et al. (2009))

Different biomass-derived fuels or biofuels, can be represented as $C_xH_yO_z$. The overall reforming reaction of $C_xH_yO_z$ compounds can be written as follows (Xuan et al., 2009):



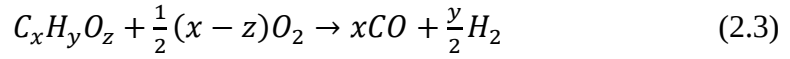
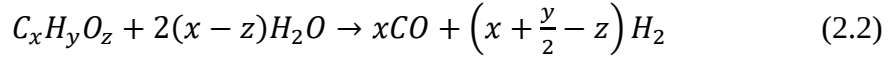
In general, hydrogen from biofuels can be produced by steam reforming (SR), partial oxidation (POX), and auto-thermal Reforming (ATR) reactions (Xuan et al., 2009). Table 2.4 shows the hydrogen production reactions and features of biomass-derived biofuels.

Table 2.4 Main reactions and features of hydrogen production from biofuels

Biofuels	Features	Ref.
Biomethanol Methanol Steam Reforming: $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ Methanol Decomposition: $CH_3OH \rightarrow CO + 2H_2$	- Liquid state in ambient conditions - High carbon/hydrogen ratio (ratio of 1:4) and unrequired C-C bonds cleavage - Low cost, easy utilization, non-toxicity and safety	Xuan et al., 2009; Ma et al., 2016; Wichert et al., 2016; Saidi et al., 2017
Biogas Methane Steam Reforming: $CH_4 + H_2O \rightarrow CO + 3H_2$ Methane Dry Reforming: $CH_4 + CO_2 \rightarrow 2CO + 2H_2$	- Basically a combination of methane and carbon dioxide - It can be used as a fuel in cogeneration applications that generate power and thermal energy	Nalbant and Colpan, 2020; Esposito et al., 2019; Iulianelli et al., 2015
Bioethanol Ethanol Steam Reforming: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2$ Ethanol Decomposition: $C_2H_5OH \rightarrow CH_4 + CO + H_2$	- Bio-ethanol production technologies are more mature than bio-methanol production technologies - Better power density, non-toxicity, favorable storage, and transportation (e.g., cars and buses operating at partial load) properties than the biomethanol - More complicated multistep reaction mechanism and poorer reaction kinetics on catalyst surface than methanol	Xuan et al., 2009; Guo et al., 2008; Iulianelli and Basile, 2020a
Biodiesel Biodiesel Steam Reforming: $C_{19}H_{36}O_2 + 17H_2O \rightarrow 19CO + 35H_2$ Biodiesel Decomposition: $C_{19}H_{36}O_2 \rightarrow 17C + 2CO + 18H_2$	- Non-toxic and biodegradable and easier to reform to high quality hydrogen rich gas - Around 1673 K, hydrogen production from biodiesel can occur without catalyst. At lower temperatures, catalyst can be used in order to activate the reaction. - Poorer carbon chains than the original oils.	Xuan et al., 2009; Sgroi et al., 2005; Bagnato et al., 2017
Bioglycerol Glycerol Steam Reforming: $C_3H_8O_3 + H_2O \rightarrow 3CO + 4H_2$	- High energy density - Non-toxic, non-volatile, and non-flammable - A byproduct of biodiesel production - Its hydrogen selectivity is much less than ethanol at the same conditions.	Xuan et al., 2009; Bagnato et al., 2017; Ketchie et al., 2007; Valliyappan et al., 2008; Iulianelli et al., 2011

As stated above, steam reforming of methane is the most used process for hydrogen production; however, this process requires a lot of heat due to the large endothermic nature of this reaction. In partial oxidation, the fuel stream is partially burned with oxygen or air. This reaction is exothermic; therefore the calorific value of hydrogen is lower than the original feedstock. The general forms of steam reforming and partial

oxidation reactions of $C_xH_yO_z$ compounds are given in Eqs. (2.2) and (2.3), respectively.



In the present time, ammonia is produced on a large scale (over 100 million tonnes per year) from fossil fuels (Bell and Torrente-Murciano, 2016). However, sustainable production of ammonia from renewable resources (e.g., solar, wind, geothermal, or hydro) and waste heat combined with biomass or organic waste (Zamfirescu and Dincer, 2009; Lan et al., 2012) is also possible. Ammonia has some advantages such as easy liquefaction, no carbon dioxide emission, already established transport and storage mechanisms, and high energy densities as both weight-based and volume-based (Zamfirescu and Dincer, 2009; Hayakawa et al., 2019). However, the ammonia decomposition reaction given in Eq. (2.4), proposed by Green (1982), should occur at low temperatures (in the range of 300-400°C) since this reaction is kinetically limited, even if not thermodynamically (Bell and Torrente-Murciano, 2016; Itoh et al., 2021).



Some studies related to hydrogen production from renewable fuels using membrane reactors are found in the literature. Table 2.5 summarizes these studies conducted in the last decade according to the reactor type, reforming process, operating conditions, and their important results. According to Table 2.5, in the studies related to SR of biogas, it was shown that operating temperature and pressure changes from 450°C to 827°C and from 1 bar to 2 bar, respectively. Also the fuel conversion increases with the enhancement of the operating temperature. For the studies on SR of methanol, it was shown that operating temperature and pressure were approximately 300-400°C and 1.5-2 bar, respectively. Moreover, it was demonstrated that the fuel conversion at the same temperature increases with an increase in pressure (from 1.5 to 2 bar), and the hydrogen recovery was approximately 60-65%. In the studies related to SR of ethanol, at the same operating temperature and pressure (400°C and 2 bar) for the Pd-

based membrane reactor and catalytic Pd-Ag membrane reactor, the fuel conversion changes from 99.5% to 94%; and also hydrogen recovery changes from 84% to 70%. In addition, when a FBMR is compared to a PBMR, the operating temperature and pressure are higher; whereas the values of fuel conversion and hydrogen recovery are lower. The studies on SR of glycerol showed that the values of fuel conversion and hydrogen recovery for a sorption-enhanced membrane reactor decrease with an increase in the operating pressure. Moreover, at the same operating conditions, when the sorption-enhanced membrane reactor is compared with dense Pd-Ag membrane reactor, it was found that the values of fuel conversion and hydrogen recovery for the dense Pd-Ag membrane reactor were higher. The studies on ammonia decomposition showed that operating temperature and pressure change from 400°C to 520°C and from 2 bar to 5 bar, respectively. In addition, fuel conversion and hydrogen recovery at the same pressure increase when operating temperature also increases.

2.4 Reforming Processes Used for Hydrogen Production from Biogas

The reforming processes for hydrogen production from biogas or methane can be split into two as the conventional and non-conventional reforming processes. The conventional reforming processes are mainly known as steam reforming (SR), partial oxidation reforming (POR), auto-thermal reforming (ATR), dry reforming (DR), and dry oxidation reforming (DOR). The non-conventional reforming processes are known as solar reforming, catalytic decomposition, and thermal plasma reforming (Verma and Samanta, 2016).

Hydrogen can be generated by reforming of biogas or methane in a wide range of temperature (600-1000°C) through endothermic or exothermic and reversible reactions. These reforming reactions generally occur at low pressure. In various reforming processes, biogas that is mainly a mixture of methane and carbon dioxide is reacted with agents such as steam, air or oxygen to produce syngas including hydrogen and other gases (Galvagno et al., 2013). Figure 2.5 shows the main steps of hydrogen production from biogas.

Table 2.5 Overview of the studies on hydrogen production from renewable fuels through membrane reactors

Membrane Reactor Type	Reforming Process	Operating Conditions	H ₂ Recovery	Fuel Conversion	Ref.
Pd-Al ₂ O ₃ membrane reactor	SR of biogas	450°C; 2 bar	70%	30%	Iulianelli et al., 2015
Pd-Ag membrane reactor	SR of biogas	837°C; 1 bar	-	89.9% CH ₄ ; 99.9% CO ₂	Balaji et al., 2020
Multifunctional membrane reactor	SR of biogas	550°C; 1 bar	80%	~30% CH ₄ ~45% CO ₂	Parente et al., 2020
Catalytic Pd-Ag membrane reactor	SR of methanol	300°C; 2 bar	64%	94%	Saidi, 2017
Pd-Cu alloy membrane reactor	SR of methanol	400°C	60%	-	Mironova et al., 2020
Silica membrane reactor	SR of methanol	300°C; 1.5 bar	-	85%	Ghasemzadeh et al, 2015
Packed bed membrane reactor	SR of ethanol	400°C; 3 bar	65%	98%	Iulianelli et al., 2016a
Pd-based membrane reactor	SR of ethanol	400°C; 2 bar	70%	99.5%	Iulianelli et al., 2018
Catalytic Pd-Ag membrane reactor	SR of ethanol	400°C; 2 bar	~84%	~94%	Saidi et al., 2018
Fluidized membrane reactor	SR of ethanol	577°C; 10 bar	~45%	~50%	Gallucci et al., 2010
Dense Pd-Ag membrane reactor	SR of glycerol	400°C; 5 bar	60%	57%	Iulianelli et al., 2011
Sorption-enhanced membrane reactor	SR of glycerol	300-500°C; 1-5 bar	86%	88%	Macedo et al., 2019
Sorption-enhanced membrane reactor	SR of glycerol	400°C; 4.5 bar	40-60%	10%	Silva et al., 2019
Catalytic composite membrane reactor	Ammonia decomposition	500°C; 5 bar	91%	>99%	Park et al., 2020
Catalytic membrane reactor	Ammonia decomposition	450°C; 2 bar	-	50%	Di Carlo et al., 2011
Catalytic membrane reactor	Ammonia decomposition	400°C; 5 bar	87.5%	98%	Zhang et al., 2019
Packed bed membrane reactor		520°C; 3 bar	66%	98%	

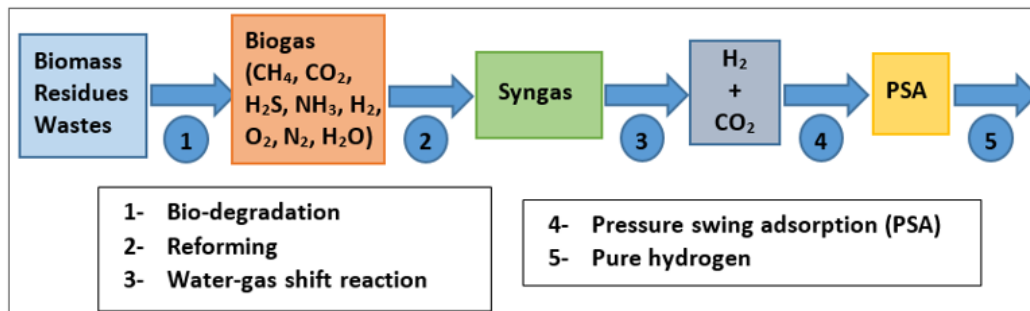


Figure 2.5 Main steps of hydrogen production from biogas (Adapted from Minh et al. (2018))

Before the biogas reforming process, undesirable and toxic substances (H_2S) in the biogas must be removed using some purification techniques; 1) physicochemical treatment such as the production of metal sulfide with chemical adsorption of H_2S on the solid adsorbent and absorption in hydrated solutions, and 2) biological treatment, for example, the living microorganisms like bacteria eliminates impurities with converting harmful toxic substances into less harmful forms (Verma and Samanta, 2016; Alves et al., 2013; Holladay et al., 2009). Consequently, reactions for the biogas reforming are similar to those for the methane reforming. Table 2.6 shows the chemical reactions formed in reforming processes and its enthalpy of reaction at $25^\circ C$ and 1 atm.

Table 2.6 Chemical reactions formed in reforming processes (Verma and Samanta, 2016; Alves et al., 2013)

Eqs. No	Reaction Name	Chemical Reaction	ΔH_{298} (kJ/mol)
Eq. (2.5)	Steam reforming	$CH_4 + H_2O \rightarrow CO + 3H_2$	206
Eq. (2.6)	Water-gas shift reaction	$CO + H_2O \rightarrow CO_2 + H_2$	-41.2
Eq. (2.7)	Combined reaction	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	165
Eq. (2.8)	Methane cracking	$CH_4 \rightarrow C + 2H_2$	74.9
Eq. (2.9)	Boudouard reaction	$2CO \rightarrow C + CO_2$	-172.4
Eq. (2.10)	Reduction of CO	$CO + H_2 \rightarrow C + H_2O$	-131.3
Eq. (2.11)	Partial oxidation reforming	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	-35.6
Eq. (2.12)	Complete oxidation	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-801.7
Eq. (2.13)	Auto-thermal reforming	$CH_4 + x/2O_2 + yCO_2 + (1-x-y)H_2O \rightarrow (y+1)CO + (3-x-y)H_2$	~ 0
Eq. (2.14)	Dry reforming	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$	247.4
Eq. (2.15)	Dry oxidation reforming	$CH_4 + \beta CO_2 + (1-\beta)/2O_2 \rightarrow (1+\beta)CO + 2H_2$	$(285\beta-38), 0 < \beta < 1$

2.4.1 Steam Reforming (SR)

Steam reforming reaction is highly endothermic and the required temperature for high H_2 yields (60-70%) is in between 650 and $850^\circ C$. Although it needs significant external energy input, it is the most widely used method for producing hydrogen in industrial applications. Steam reforming process involves steam reforming, water-gas shift, and direct steam reforming reactions. Firstly, methane reacts with water in the SR, and the syngas including carbon monoxide and hydrogen is produced in the presence of suitable catalyst (Eq. (2.5) in Table 2.6). After that, the syngas is cooled down to a temperature between 300 and $500^\circ C$ and fed to the WGS reactor where

carbon monoxide reacts with water to reduce CO content in the syngas, and carbon dioxide and hydrogen are produced (Eq. (2.6) in Table 2.6). WGS reactor includes high-temperature (HT) and low-temperature (LT) water-gas shift reactors. HT-WGS reactor has high CO conversion and low reaction kinetics; whereas LT-WGS reactor has low CO conversion and high reaction kinetics (Minh et al., 2018). The used catalysts in the WGS are Fe, Mo, Cu, and Fe-Pd alloys [4]. In addition, direct steam reforming reaction (Eq. (2.7)) or combined reaction, which is the sum of Eqs. (2.5) and (2.6), occurs. To produce highly pure hydrogen in SR, the separation unit such as PSA or membrane is needed to remove CO₂, CO, and other gases (except hydrogen) from syngas. Figure 2.6 shows the schematic diagram of the steam reforming process including reactants and products.

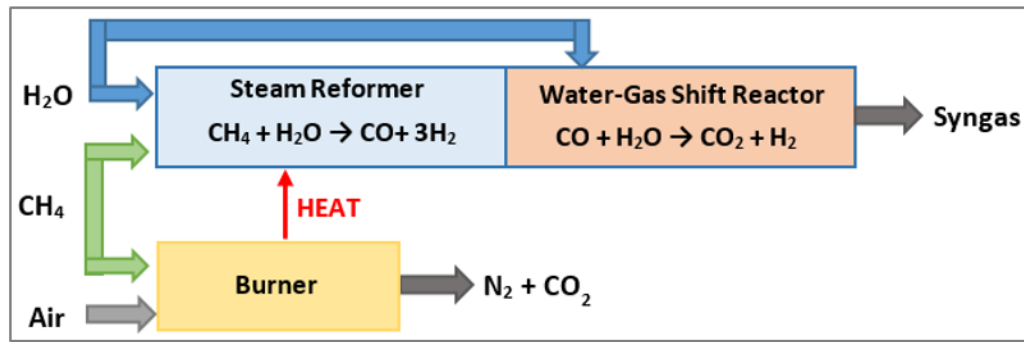


Figure 2.6 Schematic diagram of steam reforming process including reactants and products

In some cases, parallel reactions that cause carbon formation on the catalytic surface can occur such as methane cracking (Eq. (2.8)), Boudouard (Eq. (2.9)), and CO reduction reactions (Eq. (2.10)). When the carbon formation appears as the form of nanotube, it provides lower dispersion of carbon over the catalyst surface, consequently, the catalyst activity is preserved for a longer time.

In SR, the reaction temperature, the molar rate of H₂O/CH₄, and reaction pressure are the critical operating parameters. Let's consider two cases; (i) Case A: 1 mole of H₂O and 1 mole of CH₄, and (ii) Case B: 3 mole of H₂O and 1 mole of CH₄. When the case A is considered, the production of hydrogen occurs when the temperature exceeds 180°C; the CO₂ and solid carbon that are undesirable byproducts are observed at 250-800°C and 450-800°C, respectively. When the Case B is considered, solid carbon

formation is eliminated and CH₄ is completely consumed above 720°C. Considering this temperature level, Case B seems to be more advantageous than Case A. Thus, when the reaction temperature and the molar rate of H₂O/CH₄ increase, the conversion of CH₄ increases and the carbon formation decreases. In addition, when the reaction pressure increases, the molar flow rate of hydrogen decreases and the molar flow rate of CH₄ increases, thus, the conversion of CH₄ decreases (Minh et al., 2018).

Another critical parameter is the type of catalyst. Catalyst can be some transition metals (Ni, Fe, Co, Mo etc.) and noble metals (Pd, Ru, Pt, Ir, Rh etc.). For example, Kikuchi et al. (1974) reported that reactivity of metals is in the following order for steam reforming of methane: Fe=Co<Pt=Pd<Ir<Ni<Ru=Rh (Kikuchi et al., 1974). The most used metal is Ni due to its lower cost. However, Ni is less resistant to the formation of coke, therefore, Pt and Pd are more attractive for the stability of catalyst. Rh is used in the event of mass transfer limitations, since it has better activity and provides lower formation of coke (Alves et al., 2013; Iulianelli et al., 2010).

2.4.2 Partial Oxidation Reforming (POR)

The partial oxidation reforming for producing hydrogen decreases the cost of energy because of its moderately exothermic reaction. At the atmospheric pressure, methane is partially oxidized with oxygen, and the syngas including hydrogen and carbon monoxide is produced (Eq. (2.11) in Table 2.6). Figure 2.7 shows the schematic diagram of partial oxidation reforming process including reactants and products.

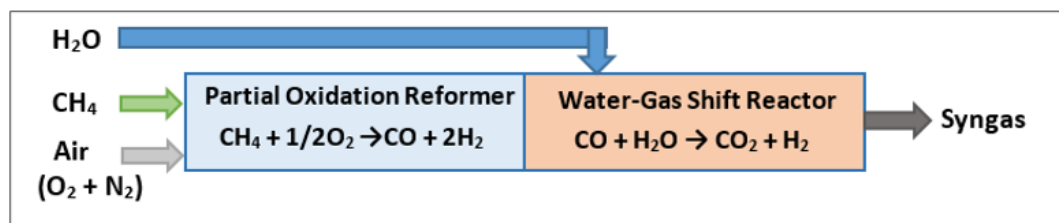


Figure 2.7 Schematic diagram of partial oxidation reforming process including reactants and products

To provide highly CH₄ conversion and to reduce the formation of coke, the required temperature should be between 700 and 900°C. In addition, if the selectivity of carbon

monoxide decreases slightly, methane can react with oxygen to produce CO₂, which is called as complete combustion reaction (Eq. (2.12) in Table 2.6). This reaction is a strong exothermic reaction that can cause hot spots in the reactor bed and the formation of coke on the catalytic surface (Alves et al., 2013; Dantas et al., 2012).

The oxidation reforming process can be realized with or without catalyst (Ahmed and Krumpelt, 2001; Rohendi et al., 2018). Recently, researchers have investigated stability and activity of several catalysts for POR. At high temperatures (>800°C), the solid solutions of Ni-Mg-Cr-La-O, NiO-MgO, and Ca-Sr-Ti-Ni and mixed metal oxides, which are used as catalysts, ensure higher coke formation resistance (Verma and Samanta, 2016; Alves et al., 2013).

2.4.3 Auto-Thermal Reforming (ATR)

Auto-thermal reforming is defined as the combination of partial oxidation reforming (Eqs. (2.11) and Eqs. (2.12) in Table 2.6) and steam reforming (Eq. (2.7) in Table 2.6). In ATR, the heat generated from partial oxidation reaction is used for the needed heat in the highly endothermic steam reforming reaction. The external heating is not required; therefore, ATR provides more efficiently and economical hydrogen production. Figure 2.8 shows the schematic diagram of auto-thermal reforming process including reactants and products.

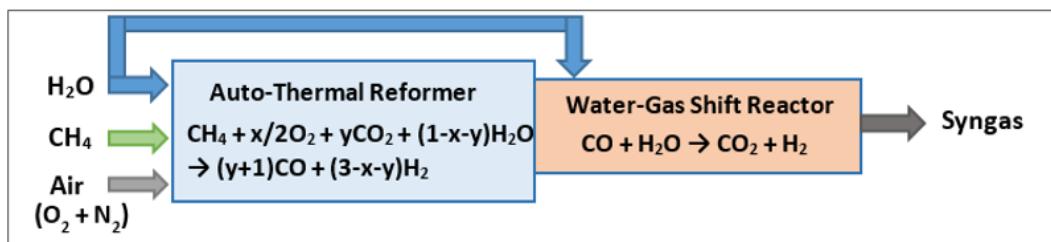


Figure 2.8 Schematic diagram of auto-thermal reforming process including reactants and products

ATR has some advantages such as faster reforming processing and higher H₂/CO ratios in comparison to POR. The generation of desired product is provided by different feed ratio combinations of CH₄-H₂O-O₂. Moreover, the control of temperature during the process can be advanced by the combination of steam

reforming and partial oxidation reforming reactions. Consequently, hot-spots formation causing the coke formation on the catalyst surface is also reduced (Verma and Samanta, 2016; Alves et al., 2013). To produce hydrogen from biogas, the range of ratios for $\text{H}_2\text{O}/\text{CH}_4$, O_2/CH_4 , and H_2/CO can be taken as 1-2.5, 0.25-0.55, and 2-3.5, respectively (Mosayebi et al., 2012).

2.4.4 Dry Reforming (DR)

In DR, methane reacts with carbon dioxide to produce syngas consisting of hydrogen and carbon monoxide (Eq. (2.14) in Table 2.6). Figure 2.9 shows the schematic diagram of dry reforming process including reactants and products. This reaction type can be attractive considering the environmental issues, because two main greenhouse gas types (CH_4 and CO_2) are consumed in DR. Contrarily, the needed heat for the endothermic DR reaction is generated with the burned fuels, which causes the CO_2 emissions to the atmosphere.

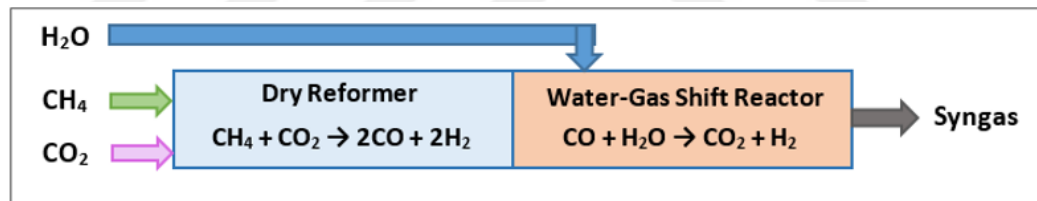


Figure 2.9 Schematic diagram of dry reforming process including reactants and products

The other parallel reactions such as reverse water-gas shift reaction (Eq. (2.6) in Table 2.6), methane cracking reaction (Eq. (2.8) in Table 2.6), and Boudouard reaction (Eq. (2.9) in Table 2.6) can change the equilibrium conversion in the major reaction. Generally, the temperature of DR process is between 700 and 900°C and the molar ratio of CH_4/CO_2 is between 1 and 1.5 (Alves et al., 2013).

The major problem in DR process is the carbon accumulation or coke formation on the catalyst surface. The parallel reactions can cause tendency of coke formation that affects the activation of catalyst. For example, when the removal rate of carbon is lower than the methane cracking, the carbon formed as a result of the methane cracking

reaction accumulates and causes an important problem like coke formation. Moreover, the Boudouard reaction that is favorable at low temperatures promotes the methane cracking reaction in order to produce additional carbon, since this reaction is exothermic in nature (Verma and Samanta, 2016; Alves et al., 2013).

The most effective catalysts used in DR process have been investigated by some researchers, and they report several metals that belong to 8, 9, and 10 groups in the Periodic Table, such as Ru, Pt, and Rh. These catalysts are very expensive, and their availability is limited in nature; therefore, they are not appropriate for industrial applications. Other catalysts that have cheaper and higher resistance of coke formation have been investigated, such as Ni and Co (Verma and Samanta, 2016; Bereketidou and Goula, 2012)

2.4.5 Dry Oxidation Reforming (DOR)

Dry oxidation reforming is defined as the combination of partial oxidation reforming (Eqs. (2.11) and Eqs. (2.12) in Table 2.6) and dry reforming (Eq. (2.14) in Table 2.6). Furthermore, DOR provides the control of carbon formation on the catalyst surface, because the carbon accumulated in DR reactions can react with oxygen, and carbon including gases (CO or CO₂) can be produced. Figure 2.10 shows the schematic diagram of dry oxidation reforming process including reactants and products. β is defined as the stoichiometric ratio of CO₂ fed with conventional DR. If β is taken as 1, this reaction will be non-oxidative DR reaction, whereas if β is taken as 0, this reaction will be a partial oxidation reaction. Therefore, the value of β should be taken between 0 and 1 (Alves et al., 2013).

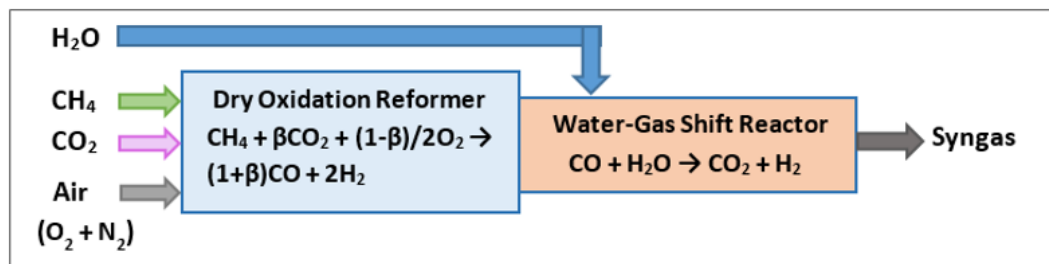


Figure 2.10 Schematic diagram of dry oxidation reforming process including reactants and products

Additional advantages of DOR where CH_4 is fed with O_2 and CO_2 are as follows: improved resistance of deactivation, increased stability of catalyst, advanced CH_4 conversion, decreased overall energy related to the process, and enhanced hydrogen yield at low temperatures.

In the DOR, some critical parameters such as the temperature of reaction and/or the concentration of oxygen feed cause a change in the ratio of H_2/CO and reaction nature as endothermic or exothermic. As known, POR reaction (Eq. (2.11) in Table 2.6) is exothermic while DR reaction (Eq. (2.14) in Table 2.6) is endothermic. Hence, the process of DOR, in which oxygen with different molar ratios can be fed at various temperatures, could be an alternative to the conventional DR process. In addition, oxygen feed decreases the formation of coke on the catalyst surface and provides better control for the partial oxidation to produce CO or CO_2 formations. Consequently, the syngas production from biogas from this process has higher energy efficiency requiring less external energy (Alves et al., 2013 ; Avraam et al., 2010). Recent studies have focused on catalysts (e.g., Ni) that includes a second metal support to increase the stability of catalyst (Verma and Samanta, 2016; Lau et al., 2011). Table 2.7 presents the summary of the comparison of the reforming processing methods discussed above.

2.4.6 Considerations for Producing Hydrogen from Biogas Reforming Technologies

Reforming processing method used to produce hydrogen can be selected depending on the composition of biogas, availability of investment, required hydrogen purity, and the amount of desired hydrogen (Alves et al., 2013 ; Scarlat et al., 2018). Biogas as a fuel cannot be directly used in conventional reforming processes. H_2S content in biogas causes a rapid reduction in the activity of catalyst due to its poisoning effect. Therefore, some purification methods such as adsorption, membrane technologies, and biological methods are used to remove H_2S .

The chemical composition of treated biogas involves mainly CH_4 and considerable CO_2 . Therefore, CO_2 naturally present in the biogas can be used as an oxidant to react

with CH₄ in dry reforming. Nevertheless, if the ratio of CO₂/CH₄ in biogas is lower than 1 (as it generally occurs), the addition of alternative oxidant is required to produce syngas that consists of hydrogen and carbon monoxide. This situation leads to the addition of oxygen through dry oxidation reforming, which could be considered as a more suitable method than DR for hydrogen production from biogas. This reforming process also slightly increases the ratio of H₂/CO (Alves et al., 2013).

The main challenges in all reforming processes are to choose suitable catalyst that prevents the carbon formation on its active surface and to increase the useful life of catalyst. The carbon formation problem is critical for DR process, since the parallel reactions occurred in DR cause the carbon formation to increase. Therefore, the hydrogen production from biogas in DR is unfeasible because of the fast deactivation of the catalyst. On the other hand, DOR process can be suitable for the elimination of carbon formation, because additional O₂ feed helps the gasification of carbon, thus the availability of catalytic active surface is enhanced. However, the ratio of H₂/CO in both DR and DOR processes is approximately equal to 1, thus it limits the high purity potential of hydrogen produced by WGS reactor, since the volume of produced CO is high. In addition, the part of hydrogen produced using dry reforming process can react with carbon dioxide via the reverse water-gas shift reaction (Eq. (6) in Table 2.6), consequently, water and carbon monoxide are produced, and the hydrogen yield is reduced. The above discussion shows that both DR and DOR processes are not quite suitable and feasible for producing hydrogen from biogas (Alves et al., 2013).

Table 2.7 Comparison of reforming processing methods

Methods	Advantages	Disadvantages	Comments
SR	• Low carbon formation • Production of highly pure hydrogen	• Need to add water vapor • High external energy requirement • High operating temperature • Expensive catalyst	• Widely used to produce hydrogen in industrial applications
POR	• Relatively low operating temperature • High energy efficiency	• Formation of hot spots in the catalytic bed with increasing temperature • May completely oxidize methane if CO selectivity is decreased	• Can be combined with other reforming methods • Limited industrial applications
ATR	• Production of highly pure hydrogen • High energy efficiency • No need for external heat • Lower cost • Can be stopped and restarted	• Complex control process • Requires multiple catalysts • Can be unstable	• Combination of POR and SR • ATR improves the temperature control and reduces the formation of hot spots • Self-sustaining process
DR	• High conversion efficiency • Environmentally friendly process (CH₄ and CO₂ are consumed)	• Carbon formation • Parallel reactions consume hydrogen • High operating temperature • High energy demand • Expensive catalyst	• Can utilize CH₄ and CO₂ that are in biogas
DOR	• Less carbon formation • Reduced overall energy involved • High conversion efficiency • Increased stability of catalyst and deactivation resistance	• Complex control process • High CO₂ production • A second metal is required for the stability of the catalyst	• Combination of POR and DR • Can be an endothermic or exothermic reaction according to O₂ feeding

Before almost all reforming processes, biogas should be purified from H₂S, and the chemical composition of biogas becomes 93-96% of methane, 4-7% of carbon dioxide, and <20 ppm of H₂S. Low CO₂ content in the biogas enhances CH₄ conversion and provides higher hydrogen purity. However, for both DR and DOR processes, CO₂, which is the reactant matter should be added. Therefore, SR, POR, and ATR processes

are more suitable than DR and DOR processes (Alves et al., 2013). ATR process can be appeared as an attractive path for hydrogen production from biogas, since this process provides high energy efficiency and high hydrogen yield. Moreover, ATR can be rapidly stopped and restarted due to self-sustaining process, resulting in the lowest ratio of expense/utility compared to all the other reforming processes. ATR has complex control process since it can be unstable (Alves et al., 2013). SR process could be seen to be a less advantageous method due to the need of high external heat, but it can be a more feasible solution if appropriate conditions are selected. In SR reactor, syngas is produced from biogas, and followed by WGS reactor to minimize the CO content in the syngas. This technology is better known and controlled. Therefore, SR is the most widely used method for producing hydrogen in industrial applications (Alves et al., 2013).

Generally, hydrogen is produced using the conventional steam reforming process that involves a reformer, a WGS reactor, and a separation unit. On the other hand, membrane reactors that allow both hydrogen production and purification in the single reactor at the same time have recently become the focus of interest for producing hydrogen from biogas as discussed in the following section.

2.4.7 Current Status of Hydrogen Production from Biogas

Biogas produced with degradation of organic materials by microorganisms is a renewable fuel that could be used the production of clean fuel like hydrogen. The interest in hydrogen production from biogas is gradually increasing. In the last 5 years in the literature, the hydrogen production from biogas with conventional reformer have been investigated in detail. For example, Chattanathan et al. (2014) investigated the effects of H₂S concentration (0.5, 1.0 and 1.5 mol %) and temperature (650, 750 and 850°C) on the CH₄ and CO₂ conversions during biogas dry reforming process. The results showed that even with presence of little H₂S strongly decreased the CH₄ and CO₂ conversions compared to the absence of H₂S. When the concentration of H₂S increases from 0 to 0.5 mol%, the CH₄ and CO₂ conversions decrease from 67% and 87% to 19% and 22%, respectively. Izquierdo et al. (2014) investigated the effects of

different catalysts that are Ni and Rh-Ni supported on Zeolites L (disc and cylindrical morphologies) to production hydrogen from biogas for different reforming processes such as dry reforming, steam reforming, oxidative reforming, and tri-reforming. In the SR, type of disc catalyst was found as more active at low S/C ratio. On the other hand, in the DR, the type of cylindrical catalyst was found as more active. Furthermore, the catalyst with Rh presented better reforming performance for all reforming processes and conditions. Consequently, the most promising catalyst was found as Rh-Ni catalyst based on especially cylindrical Zeolite L. Cipiti et al. (2016) developed a mathematical model to test biogas steam reforming reactor. The effects of inlet temperature and the molar ratio of reactants on the performance of reactor were investigated with parametric analysis, then this model was validated with experimental data for Ni/CeO₂ catalyst and 700-900°C of temperature. At the S/C=3, when the temperature increases from 700 to 900°C, CH₄ conversion and H₂/CO changes from 65.4 to 99.7% and from 4.5 to 2.8, respectively. At 900°C, when the S/C increases from 1 to 5, CH₄ conversion and H₂/CO changes from 99.3 to 98.6% and from 1.6 to 3.8, respectively. Pawar et al. (2017) studied the biogas dry reforming and investigated the catalyst deactivation that is formed by poisoning of Sulphur and coke formation. This study was examined for different CH₄/CO₂ ratio (1.5 and 2), temperature (700-800°C), and H₂S content in biogas (0, 5, and 10 ppm). The results show that the catalyst deactivation faster realized in the presence of Sulphur. At 700°C, the deactivation is not reversible, while at 800°C, the catalyst activation is recovered with removing Sulphur in the biogas feed. Moreover, the dry reforming of biogas leads to the carbon formation as multi-walled nanotubes for this conditions. Tuna et al. (2018) evaluated the catalyst used in biogas steam reformer. In this study, two type catalyst that are 7.4% Ni/NiAl₂O₄/g-Al₂O₃ and 3.1% Ru/g-Al₂O₃ are studied. These catalysts showed high H₂ and CO selectivity, high CH₄ conversion, high resistance for carbon formation, zero production of CO or CO₂, and low deactivation. The temperatures of 7.4% Ni/NiAl₂O₄/g-Al₂O₃ and 3.1% Ru/g-Al₂O₃ catalysts are 850°C and 700°C, respectively. Calgora and Perez-Lopez (2019) evaluated Ni-M-Al catalysts used in hydrogen production from synthetic biogas (70% of CH₄ and 30% of CO₂) by dry reforming. This catalyst involving 55% of Ni, 33% of Al and 11% of third component (M, Mg, Ca, Cu, Li, La, Zn, Co) was investigated with

varying of third component. The catalyst including La provided greater stability in reforming reactions because of its high sintering resistance and strong sites of acid.

On the other hand, the interest in hydrogen production via membrane reactor increases due to some advantages mentioned above compared to conventional reactors. However, most of studies in the literature were found related to hydrogen production from methane via membrane reactor. There are very few studies related to hydrogen production from biogas using membrane reactor. For example, Silva et al. (2015) developed the mathematical model of a fixed bed membrane reactor that use Pd-Ag hydrogen selective membrane for hydrogen production from biogas. The results show that the yields of hydrogen and carbon monoxide is similar at below 873 K for conditions both with and without permeation of hydrogen. At 873 K and with permeation of hydrogen, the methane conversion and hydrogen yield were found as 83% and 113% higher than that for condition without permeation of hydrogen. In addition, the hydrogen yields at 823 K and 873 K were calculated as 21% and 47%, respectively, under permeation of hydrogen conditions. Iulianelli et al. (2015) investigated biogas steam reforming for clean hydrogen production through membrane reactor that consists of Pd/Al₂O₃ membrane. In this study, at 380°C, H₂O:CH₄=3:1:, and 2 bar, the permeate purity of hydrogen is approximately found as 96%, although methane conversion and hydrogen recovery is 15% and >20%, respectively. On the other hand, at 450°C, H₂O:CH₄=4:1:, and 3.5 bar, methane conversion and hydrogen recovery increase up to more than 30% and 70%, respectively. De Nooijer et al. (2018) investigated a fluidized bed membrane reactor that provides pure hydrogen production from biogas with steam reforming, and developed the one-dimensional and two-phase model of fluidized bed membrane reactor. This model was validated with experimental data for 435-535°C, 2-5 bar, and the ratio of CO₂/CH₄ up to 0.9. Table 2.8 presents the summary of the studies on the different H₂ production methods using biogas and reaction conditions in the literature.

Table 2.8 The summary of the studies on the different H₂ production methods using biogas and reaction conditions

Methods	Reactor Type	Biogas Composition	T (°C)	Catalyst	H ₂ /CO	X _{CH₄}	Ref.
DR	CR (fixed bed)	59% CH ₄ , 2%N ₂ , and 39% CO ₂	800	Reformax®250	0.98	67%	Chattananathan et al., 2014
SR DR POR	CR (fixed bed)	60% CH ₄ and 40% CO ₂	800	Rh-Ni based on cylindrical Zeolite L	1.6 0.9 1.1	86% 65% 90%	Izquierdo et al., 2014
SR	CR (fixed-bed)	60% CH ₄ and 40% CO ₂	900	7.5-wt.%Ni/CeO ₂	2.8	99.7	Cipiti et al., 2016
DR	CR (fixed-bed)	60% CH ₄ and 40% CO ₂	700 800	Ni/-Al ₂ O ₃	~1.118 ~1.2	~65% ~72%	Pawar et al., 2017
SR	CR (fixed bed)	60% CH ₄ and 40% CO ₂	700 850	3.1% Ru/g-Al ₂ O ₃ 7.4% Ni/NiAl ₂ O ₄ /g-Al ₂ O ₃	3 2.9	60% 60%	Tuna et al., 2018
DR	CR (fixed bed)	70% CH ₄ + 30% CO ₂	500 700	Ni-La-Al	2.6 5.2	35% 75%	Calgaro and Perez-Lopez, 2019
SR	MR (fixed bed)	74% CH ₄ + 26% CO ₂	600	Ni (3.31% weight)/γ-Al ₂ O ₃)	-	47%	Silva et al., 2015
SR	MR (fixed bed)	60% CH ₄ and 40% CO ₂	380 450	Ni(25 wt%)/Al ₂ O ₃	-	15% 34%	Iulianelli et al., 2015
SR	MR (fluidized bed)	53% CH ₄ and 47% CO ₂	435 535	-	-	30% 70%	de Nooijer et al., 2018

2.5 Kinetics of Steam-Methane Reforming Reactions

In this section, different reaction kinetic expressions for steam-methane reforming reactions occurring in the MRs are reviewed. As it can be seen in Table 2.9, the main reactions occurring in a steam-methane reforming process are steam reforming (SR) (Eq. (2.16)), water-gas shift (WGS) (Eq. (2.17)), and direct steam reforming (DSR) (Eq. (2.18)). These reactions usually occur at the temperatures of 673-823 K in a MR, thus the coke formation (Eq. (2.19)) can be neglected at these temperature levels (Murmura et al., 2018). It is considered that the reactions given in Eqs. (2.16), (2.17), and (2.18) control the overall reaction rate for hydrogen production since they have slower reaction rates than the other reaction step given in Eq. (2.19) (Xu and Froment, 1989). In this section, firstly, a brief information on the kinetic analysis are given, then

a detailed information and discussion on the most used reaction rate expressions are examined.

Table 2.9 Main reactions occurring in a steam-methane reforming process

Reactions	Equation Number
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Eq. (2.16)
$CO + H_2O \leftrightarrow CO_2 + H_2$	Eq. (2.17)
$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	Eq. (2.18)
$CH_4 \leftrightarrow C + H_2$	Eq. (2.19)

2.5.1 Kinetic Analysis

Many studies related to the kinetic analysis models have been performed to examine the steam reforming kinetics. The first-order kinetics model that is one of them has the general agreement for most the researchers, however, the range of the activation energies was reported as very wide. The reason for this wide range can be explained by the experimental mistakes due to the limitations of diffusion and heat transports (Van Beurden, 2004). To overcome these mistakes, some studies that accept the probability of diffusion limitations have been found in the literature. For example, Xu and Froment (1989) studied the comprehensive study of the intrinsic kinetics of the steam-methane reforming and water-gas shift reactions for Ni/MgAl₂O₄ catalyst, and they developed a reaction kinetic model based on the Langmuir-Hinshelwood reaction mechanism. The detailed rate expression equations used by Xu and Froment (1989) are given in Section 2.5.2.4.

Kinetic analysis can be classified into two groups as simple power rate laws or more complex expressions such as Langmuir–Hinselwood kinetic model. In order to better understand the reaction kinetics, the development of a kinetic model based on the experimental data for methane conversion is necessary (Thattai et al., 2017). Different assumptions can be made according to the relationship between hydrogen and steam concentrations, the control steps, and the adsorption of species on the catalyst sites (Quirino et al., 2021).

2.5.1.1 Power Rate Law Expressions

Power rate law expression is a simple modeling approach that formulates the rate equation using a single-step reaction (Froment et al., 1990). The rate equation used in the power rate law expression is given in Eq. (2.20).

$$-r_{CH_4} = k \cdot P_{CH_4}^{\alpha_{CH_4}} \cdot P_{H_2O}^{\alpha_{H_2O}} \quad (2.20)$$

where P_i and α_i are the partial pressure and the reaction order, respectively. k is the rate constant, and depends on the variables which affect the rate, whereas it is independent of the concentration of species. k is calculated using the Arrhenius equation given in Eq. (2.21).

$$k = k_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (2.21)$$

where k_0 is the pre-exponential factor, E_a is the activation energy, T is the temperature, and R is the universal gas constant.

2.5.1.2 Langmuir–Hinshelwood Expressions

Langmuir–Hinshelwood kinetics that takes the adsorption and desorption on the surface of the catalyst into account is commonly used to understand the kinetics of the heterogeneous catalytic processes (Thattai et al., 2017). This rate formulation is based on the chemisorbed of all species on the surface before starting any reaction (Thattai et al., 2017). A general rate equation is expressed by the combination of three groups to be directly proportional with kinetic factor and driving force and inversely proportional with adsorption term (Thattai et al., 2017; Froment et al., 1990).

$$r = \frac{(\text{kinetic factor}) \cdot (\text{driving force})}{\text{adsorption term}} \quad (2.22)$$

The driving force, F_D , provides information about the reaction equilibrium. The driving force for steam-methane reforming reaction can be calculated as given in Eq. (2.23) with the assumption of the surface reaction.

$$F_D = 1 - \frac{P_{CO}P_{H_2}^3}{K_{eq,SMR}P_{CH_4}P_{H_2O}} \quad (2.23)$$

where $K_{eq,SMR}$ is the equilibrium constant of steam methane reforming reaction, and it is calculated using the following equation.

$$K_{eq,SMR} = \exp\left(\frac{-\Delta G_0^{SMR}}{RT}\right) \quad (2.24)$$

When the kinetic factor (k) and the adsorption term are added to the Eq. (2.24), the general rate equation changes to the following equation.

$$r = k \cdot P_{CH_4} \cdot \frac{P_{H_2O}^a}{P_{H_2}^b} \cdot \frac{F_D}{\left(1 + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} + K_{CH_4} P_{CH_4}\right)^2} \quad (2.25)$$

Xu and Froment (1989) conducted a comprehensive study on the reaction kinetics of the steam methane reforming for Ni-MgAl₂O₄ catalyst using the Langmuir–Hinshelwood rate expressions. The detailed rate expression equations used by Xu and Froment (1989) are given in Section 2.5.2.4.

2.5.2 Different Reaction Rate Expressions

Different reaction rate expressions are available in the literature. The most used ones are taken from the studies of Numagauchi and Kikuchi (1988), Hou and Hughes (2001), Wei and Iglesia (2004), and Xu and Froment (1989). Table 2.10 shows the conditions (catalyst type, reactions considered, temperature and pressure) used in each of these studies; and the reaction rate expressions are given briefly in the following subsections.

Table 2.10 Commonly used reaction kinetic expressions for the steam-methane reactions and the experimental conditions used in these studies (Adapted from Pieterse et al. (2010))

Sources	Catalyst	Reactions	Temperature and Pressure
Xu and Froment (XF) (1989)	Ni/MgAl ₂ O ₄	(2.16), (2.17), (2.18)	573–848 K / 3–15 bar
Numaguchi and Kikuchi (NK) (1988)	Ni/Al ₂ O ₃	(2.16), (2.17)	674–1160 K / 1.2–25.5 bar
Hou and Hughes (HH) (2001)	NiO/Al ₂ O ₃ (ICI 57-4)	(2.16), (2.17), (2.18)	598–823 K / 1.2–6.0 bar
Wei and Iglesia (WI) (2004)	Ni/MgO-A	(2.16), (2.17)	823–1023 K / 1–15 bar

2.5.2.1 Numaguchi and Kikuchi

According to the reaction kinetic expression proposed by Numaguchi and Kikuchi (1988), when the Langmuir-Hinshelwood and power-law type are considered together, the reaction rates can be given as a function of partial pressures. The reaction rate expressions for the reactions shown in Eqs. (2.16) and (2.17) are given as follows (Numaguchi and Kikuchi, 1988):

$$r_{1,NK} = k_{0,1,NK} \exp\left(\frac{-E_{1,NK}}{RT}\right) \frac{P_{CH_4} - P_{CH_4,eq}}{P_{CH_4}^{\alpha_1} P_{H_2O}^{\delta_1}} \quad (2.26)$$

$$r_{2,NK} = k_{0,2,NK} \exp\left(\frac{-E_{2,NK}}{RT}\right) \frac{P_{CO} - P_{CO,eq}}{P_{CH_4}^{\alpha_2} P_{H_2O}^{\delta_2}} \quad (2.27)$$

where the subscript, NK, is the abbreviation of Numaguchi and Kikuchi. α and δ are the adsorption terms in the power law for the Freundlich adsorption rate expression. P_j and $P_{j,eq}$ are the partial pressure and the equilibrium partial pressure of each species (j : CH₄, CO, H₂, CO₂, H₂O). For the Ni/Al₂O₃ catalyst, the values of $k_{0,1,NK}$, $k_{0,2,NK}$, $E_{1,NK}$, $E_{2,NK}$, α_1 , α_2 , δ_1 , and δ_2 are taken as $9.286 \cdot 10^8$, $8.688 \cdot 10^5$, 106,870 kJ/kmol, 54,531 kJ/kmol, 0, 0, 0.596, and 0, respectively. In the literature, Marra et al. (2014) used Numaguchi and Kikuchi kinetics equations to investigate hydrogen production using the RhZrO₂ catalyst. Rhodium catalyst had 7 times higher catalytic activity than nickel catalyst (NiAl₂O₃), however, it was found that the kinetic laws of steam methane reforming for nickel catalyst hold for the Rhodium catalyst too. The results showed

that the SMR reaction rate was higher than for nickel catalyst, and the activation energy used in kinetics expressions is lower than the nickel catalyst.

2.5.2.2 Hou and Hughes

The reaction kinetic expression proposed by Hou and Hughes (2001) shows that methane conversion is proportional to the partial pressure of methane and the contact time. In the derivation of the reaction rate, the relationships between the contact time and the methane conversion in steam reforming and the contact time and the conversion of methane into carbon dioxide were both considered using the second or third degree polynomial regressions. The experimental relationships for steam methane reforming at constant temperature, pressure, and steam-methane-hydrogen ratio are given as follows (Hou and Hughes, 2001):

$$X_{CH_4} = a_0 + a_1 \left(\frac{W}{F_{CH_4}} \right) + a_2 \left(\frac{W}{F_{CH_4}} \right)^2 + a_3 \left(\frac{W}{F_{CH_4}} \right)^3 \quad (2.28)$$

$$X_{CO_2} = b_0 + b_1 \left(\frac{W}{F_{CH_4}} \right) + b_2 \left(\frac{W}{F_{CH_4}} \right)^2 + b_3 \left(\frac{W}{F_{CH_4}} \right)^3 \quad (2.29)$$

where X_{CH_4} is defined as the methane conversion for steam reforming and carbon dioxide conversion into methane for reverse water-gas shift reaction. X_{CO_2} is defined as carbondioxide conversion for reverse water-gas shift reaction and methane conversion into carbon dioxide for steam reforming. a_i and b_i are the correlation coefficients, and their values can be found in the study of Hou and Hughes (2001). The disappearance rate of methane and the formation rate of carbon dioxide are obtained using Eqs. (2.30) and (2.31) as follows:

$$r_{CH_4} = \frac{dX_{CH_4}}{d\left(\frac{W}{F_{CH_4}}\right)} = a_1 + 2a_2 \left(\frac{W}{F_{CH_4}} \right) + 3a_3 \left(\frac{W}{F_{CH_4}} \right)^2 \quad (2.30)$$

$$r_{CO_2} = \frac{dX_{CO_2}}{d\left(\frac{W}{F_{CH_4}}\right)} = b_1 + 2b_2 \left(\frac{W}{F_{CH_4}} \right) + 3b_3 \left(\frac{W}{F_{CH_4}} \right)^2 \quad (2.31)$$

When this procedure is applied similarly to the reverse water gas shift reaction experiments, the disappearance rate of carbon dioxide and the formation rate of methane are obtained as follows (Hou and Hugles, 2001):

$$r_{CO_2}^* = \frac{dX_{CO_2}^*}{d\left(\frac{W}{F_{CO_2}}\right)} = a_1^* + 2a_2^* \left(\frac{W}{F_{CO_2}}\right) + 3a_3^* \left(\frac{W}{F_{CO_2}}\right)^2 \quad (2.32)$$

$$r_{CH_4}^* = \frac{dX_{CH_4}^*}{d\left(\frac{W}{F_{CO_2}}\right)} = b_1^* + 2b_2^* \left(\frac{W}{F_{CO_2}}\right) + 3b_3^* \left(\frac{W}{F_{CO_2}}\right)^2 \quad (2.33)$$

where a_i^* and b_i^* are the correlation coefficients, and their values can be found in the study of Hou and Hughes (2001).

The steam methane reforming mechanism for different conditions and catalysts includes six kinetic mechanism possibilities ($a_1, a_2, a_3, b_1, b_2, and b_3$) since the mechanism of methane/steam with the gas phase that reacts with the absorbed reactants is usually not accepted by most of researchers (Hou and Hugles, 2001; Soliman et al., 1992). $a_1, a_2, a_3, b_1, b_2, and b_3$ represent the steam absorbed on the catalyst, steam absorbed on the catalyst with dissociation, methane absorbed on the catalyst, methane absorbed on the catalyst with dissociation into hydrogen and methylene, and methane absorbed on the catalyst with dissociation into hydrogen and carbon, respectively.

Langmuir–Hinshelwood–Hougen–Watson (LH-HW) approach was used to determine the different rate equations for six kinetic mechanisms; however, five kinetic mechanisms were rejected by the model discrimination that was done later. Thus, the rate expressions for the remaining kinetic mechanism that are represented by Eqs. (2.16)-(2.18) are given below.

$$r_{1,HH} = k_{0,1,HH} \exp\left(\frac{-E_{1,HH}}{\bar{R}T}\right) \left[\frac{P_{CH_4} P_{H_2O}^{0.5}}{P_{H_2}^{1.25}}\right] \cdot \left(P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq,1}}\right) / (DEN_{HH}^2) \quad (2.34)$$

$$r_{2,HH} = k_{0,2,HH} \exp\left(\frac{-E_{2,HH}}{\bar{R}T}\right) \left[\frac{P_{CH_4} P_{H_2O}^{0.5}}{P_{H_2}^{0.5}}\right] \cdot \left(P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{eq,2}}\right) / (DEN_{HH}^2) \quad (2.35)$$

$$r_{3,HH} = k_{0,3,HH} \exp\left(\frac{-E_{3,HH}}{\bar{R}T}\right) \left[\frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{1.75}}\right] \cdot \left(P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eq,3}}\right) / (DEN_{HH}^2) \quad (2.36)$$

where the subscript, HH, is the abbreviation of Hou and Hughes. $k_{0,i,HH}$, $E_{i,HH}$, and $K_{eq,i}$ are the reaction rate constants, the activation energy, and the equilibrium constant of reactions i (1, 2, 3), respectively. $\bar{R}$ and T are the universal gas constant and the operating temperature, respectively. P_j is the partial pressure of each species (j: CH₄, CO, H₂, CO₂, H₂O). Here, DEN_{HH} is the adsorption of reacting species to active catalyst domains and is calculated as follows:

$$DEN = 1 + K_{CO}P_{CO} + K_H P_H^{0.5} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} \quad (2.37)$$

where K_j is the adsorption constant of j species on the catalyst surface and is calculated using the Van't Hoff equation. The values of all constants in Eqs. (2.34)-(2.37) can be found for different temperatures in the study of Hou and Hughes (2001). Dixon et al. (2007) used Hou and Hughes kinetics equations to simulate steam methane reforming reactions for Ni/Al₂O₃ catalyst. They carried out three-dimensional computational fluid dynamics (CFD) simulations of steam methane reforming. In their study, the effects of intraparticle such as diffusion of species, conduction, and reaction on the external flow and temperature distributions were investigated. The results showed that the temperature profile has a symmetric distribution in the non-wall fields, whereas they have strong gradients in the wall fields.

2.5.2.3 Wei and Iglesia

The reaction kinetic expression proposed by Wei and Iglesia (2004) is a simpler expression compared to the other expressions. The rate of the direct steam reforming reaction (Eq. (18)) is directly proportional to the partial pressure of methane. The value of the reaction rate was found using an approach that is based on the evaluation of the equilibrium parameter from the CH₄–CO₂ and CH₄–H₂O thermodynamic reaction data. Thus, the equilibrium parameters (η) can be calculated as follows (Wei and Iglesia, 2004):

$$\eta_1 = \frac{[P_{CO}]^2 [P_{H_2}]^2}{[P_{CH_4}] [P_{CO_2}]} \frac{1}{K_{eq,1}} \quad (2.38)$$

$$\eta_2 = \frac{[P_{CO}][P_{H_2}]^3}{[P_{CH_4}][P_{H_2O}]} \frac{1}{K_{eq,2}} \quad (2.39)$$

where P_j is the partial pressure of species j (CH_4 , CO , H_2 , CO_2 , H_2O) and $K_{eq,1}$ and $K_{eq,2}$ are the equilibrium constants for CH_4 – CO_2 and CH_4 – H_2O reactions, respectively. η value changes between 0.05 and 0.20 for the reaction conditions taken in the study of Wei and Iglesia (2004). The rate of forward turnover (r_f) is calculated as follows:

$$r_f = \frac{r_{CH_4,WI}}{(1-\eta)} \quad (2.40)$$

In addition, the rate of forward turnover can be also calculated as follows:

$$r_f = k \cdot P_{CH_4} \quad (2.41)$$

Thus, the reaction rate of methane ($r_{CH_4,WI}$) is calculated by combining the Eqs. (2.40) and (2.41).

$$r_{CH_4,WI} = k \cdot P_{CH_4} \cdot (1 - \eta) \quad (2.42)$$

Reaction kinetic expression proposed by Wei and Iglesia emphasizes the importance of the catalytic activity of metals. In order to investigate the catalytic activity of the catalyst, Zeppieri et al. (2010) investigated the steam methane reforming kinetics of a commercial Ni-based catalyst and an innovative catalyst (rhodium-perovskite) at the condition of atmospheric pressure and changing temperature between 723 K and 1020 K by using the simple and combined model suggested by Wei and Iglesia. The performances of these catalysts were compared with each other. The results showed that the rhodium-perovskite catalyst yields a higher activity and higher methane conversion for steam-methane reforming reactions than Ni-based commercial catalyst and the methane conversion value of the rhodium-perovskite catalyst is closer to the thermodynamic equilibrium value.

2.5.2.4 Xu and Froment

The other reaction kinetic expression is proposed by Xu and Froment (1989), who broadly investigated the steam methane reforming kinetics over the Ni/MgAl₂O₄ catalyst. The rate expressions for the reactions shown in Eqs. (2.16)-(2.18) are given as follows:

$$r_{1,XF} = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \left[P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq,1}} \right] / (P_{H_2}^{2.5} \cdot DEN^2) \quad (2.43)$$

$$r_{2,XF} = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) \left[P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{eq,2}} \right] / (P_{H_2} \cdot DEN^2) \quad (2.44)$$

$$r_{3,XF} = k_{0,3} \exp\left(\frac{-E_3}{RT}\right) \left[P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eq,3}} \right] / (P_{H_2}^{3.5} \cdot DEN^2) \quad (2.45)$$

where $k_{0,i}$, $K_{eq,i}$, and E_i are the pre-exponential factor, the equilibrium constant, and the activation energy for the i^{th} reaction, respectively. P_j is the partial pressure of each species (j : CH₄, CO, H₂, CO₂, H₂O). Finally, DEN is the adsorption of reacting species to active catalyst domains and is calculated as follows:

$$DEN = 1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} \quad (2.46)$$

where K_j is the adsorption constant of j^{th} species on the catalyst surface and is calculated using the Van't Hoff equation (Xu and Froment, 1989).

$$K_j = K_{j,0} \cdot \exp\left(\frac{-\Delta \bar{h}_i}{RT}\right) \quad (2.47)$$

where $K_{j,0}$ is the pre-exponential factor, $\Delta \bar{h}_i$ is the adsorption specific enthalpy, $\bar{R}$ is the universal gas constant (8.314 kJ/kmol·K), and T is the temperature. The adsorption constants used in the Van't Hoff equation can be found in the study of Xu and Froment (1989).

Recently, several researchers have conducted studies to find the most suitable catalyst that enhances the hydrogen-rich gas production. For example, Jones et al.

(2008) suggested the following order of catalytic activity: Ruthenium (Ru) > Rhodium (Rh) > Iridium (Ir) > Platinum (Pt). Although these noble metals have both high activity and ensures low carbon deposition, the most commonly used catalyst in the steam methane reforming reactions is nickel (Ni) due to its high activity, low corrosion, and low cost (Rostrup-Nielsen, 1984; Twigg, 2018). The commonly used supports for Ni catalyst include alumina, magnesia, magnesium aluminate, and calcium aluminate (Meloni et al., 2020). The literature survey conducted on the modeling of MRs showed that the most used reaction rate expression for the steam-methane reforming reactions is the one proposed by Xu and Froment (1989). The other researchers followed the study of Xu and Froment (1989) and formed their kinetic expressions. The values of constants used in these reaction rate equations can change with the used different catalyst type or operating conditions. Different values of constants (pre-exponential factor and the activation energy) used in the rate equations given in different modeling studies on hydrogen production from methane through fixed-bed MRs are shown in Table 2.11.

Table 2.11 The values of the pre-exponential factor and the activation energy for each reaction according to different catalyst type and operating conditions

Ref.	Rxn, i	Pre-exponential factor, $k_{0,i}$ [$\text{kmol} \cdot \text{bar}^{0.5} / (\text{kg}_{\text{cat}} \cdot \text{h})$]	Activation Energy, E_i [kJ/kmol]	Catalyst type	Operating Conditions
Xu and Froment, 1989	1	4.22×10^{15}	240,100	Ni/MgAl ₂ O ₄	823 K 5 bars
	2	1.95×10^5	67,130		
	3	1.02×10^{15}	243,900		
Oliveira et al., 2009	1	2.084×10^{12}	217,010	Ni/Al ₂ O ₃	747-813 K 2 bars
	2	3.36×10^7	68,200		
	3	4.67×10^{12}	215,840		
Abbas et al., 2017	1	1.87×10^{13}	257,010	NiO/a-Al ₂ O ₃	823-973 K 1 bar
	2	3.56×10^7	89,230		
	3	4.75×10^{13}	236,700		
Obradović et al., 2013	1	1.5×10^{14}	240,266	Ni-based Pellet-type	773-848 K 3.8 bar
	2	-	-		
	3	3.0×10^{12}	209,424		
	1	1.17×10^{16}	247,406	Pt/Ni/Al ₂ O ₃ Plate-type	773-848 K 1 bar
	2	-	-		
	3	2.8×10^{16}	265,177		
Chompupun et al., 2018	1	2.20×10^{11}	229,256	Ni/Al ₂ O ₃	723-823 K 3-5 bar
	2	3.23×10^7	87,502		
	3	3.96×10^8	229,705		
Halabi et al., 2010	1	5.83×10^7	83,800	Rh/Ce _{0.5} Zr _{0.5} O ₂	748-848 K 1.5 bar
	2	2.1×10^6	15,100		
	3	1.64×10^9	89,200		

2.6 Hydrogen Permeation through Membrane

2.6.1 Modeling of each hydrogen permeation step

Membranes used in the MRs should have high hydrogen selectivity, high chemical and mechanical stabilities, and low cost (Gallucci et al., 2013). In general, dense palladium (Pd) based alloys are used due to their high solubility and hydrogen permeability. However, the cost of Pd-based membranes is relatively high, and this can be reduced with the support materials such as stainless steel and ceramic (Iulianelli et al., 2016a). In addition, Pd-based membranes may suffer from surface contamination due to exposure to different contaminants such as carbon monoxide (CO), water (H₂O), ammonia (NH₃), and hydrogen sulfide (H₂S) (Paglieri and Way, 2002). Especially, when the Pd surface is exposed to hydrogen sulfide, the sulfur component blocks the hydrogen permeation sites on the Pd-based membrane. Furthermore, sulfur can be reacted with the Pd, forming Pd₄S, which causes a reduction in the hydrogen permeance and may be responsible for the membrane failure (Burke and Madix, 1990; Iulianelli et al., 2021). Another problem with continuous hydrogen exposure is that it reduces the ductility of the metals in the membrane and causes the cracking of the metal (embrittlement phenomenon) (Rogers, 1968; Yun and Oyama, 2011).

To overcome the drawbacks mentioned above, Pd can be alloyed with other metals such as Au, Ag, Cu, Ni, Pt. In addition, the support materials can be used to reduce the cost and improve the mechanical, chemical, and thermal stabilities (Anzelmo et al., 2018). There are several studies in the literature focused on the improvement of the membrane stabilities by alloying them with other elements and the support materials. For example, Anzelmo et al. (2018) studied the fabrication and performance of a Pd/Al₂O₃ composite MR to produce hydrogen from two different types of natural gas. One type had N₂ contaminant, whereas the other type had N₂ and CO₂ contaminants. Chen and Ma (2010) studied the effect of H₂S on the performances of both Pd and Pd-Au composite membranes. Ma et al. (2013) examined the effect of different Au content (4.2 wt%–16.7 wt%) on the performance of Pd-Au membranes at temperatures from

523 to 723 K. Iulianelli et al. (2019b) studied the preparation, characterization, and testing of the supported Pd-Au composite membrane. The aim of their study was to investigate the long-term stability of permeation of hydrogen through the composite membrane and to evaluate the ideal selectivities of hydrogen according to N_2 , CO_2 , CH_4 , and He.

In general, the hydrogen permeation mechanism of a thick Pd-based membrane (Pd-thickness $> 5 \mu m$) is the Solution-Diffusion mechanism (Figure 2.11) including the different steps: (1) external diffusion of hydrogen molecule to the Pd surface, (2) dissociative adsorption of hydrogen molecule on the Pd surface to hydrogen atoms, (3) dissolution of hydrogen atom into the metal bulk, (4) diffusion of hydrogen atom through the metal bulk, (5) association of hydrogen atom on the Pd surface, (6) desorption of hydrogen molecule from Pd surface, and (7) external diffusion of a hydrogen molecule from Pd surface (Yun and Oyama, 2011).

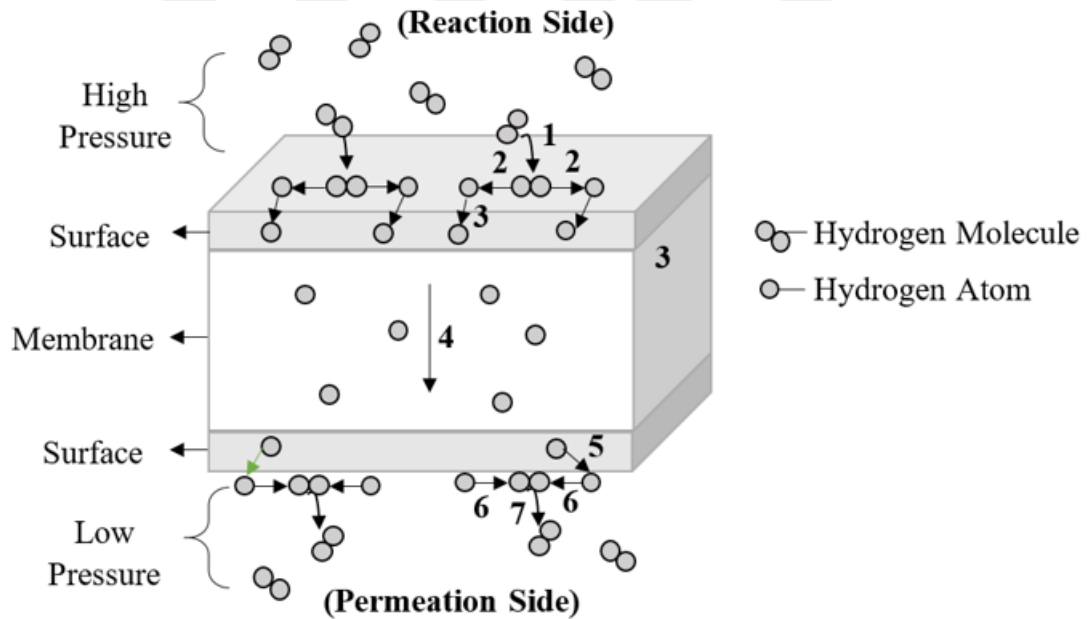


Figure 2.11 Solution-Diffusion mechanism of hydrogen permeation through Pd-based membrane

In most of the studies on MR modeling, the hydrogen flux through the membrane has been simply calculated using Sieverts' Law, which states that hydrogen flux is proportional to the difference of the square root of the partial pressure of hydrogen in the reaction side to that of hydrogen in the permeation side (Eq. (2.48)).

$$J_{H_2} = \pi(P_{H_2,react}^{0.5} - P_{H_2,perm}^{0.5}) \quad (2.48)$$

where J_{H_2} is the hydrogen permeation flux. π is the hydrogen permeance that depends on the temperature. P_j is the partial pressure of hydrogen in reaction and permeation sides. In the case of Sieverts' law, the rate-limiting step is the diffusion through the bulk and the concentration of hydrogen in the permeated stream is equal to 1, and this defines the membrane as fully hydrogen perm-selective. If the membrane is not suitable for Sieverts' law (i.e. Pd-thickness < 5 μm , presence of pin-holes, etc.), the diffusion through the membrane bulk is not the rate-determining step, and thus, the exponential coefficient, n , is not equal to 0.5, Eq. (2.49) (Yun and Oyama, 2011; Iulianelli et al., 2019b).

$$J_{H_2} = \pi_n(P_{H_2,react}^n - P_{H_2,perm}^n) \quad (2.49)$$

The pressure exponent, n , is found with a nonlinear regression, which provides to understand its difference from the ideal value (0.5) used in the Sieverts' law. Figure 2.12 shows the change of n value according to the permeation control steps and the membrane thickness at temperatures between 623 and 773K.

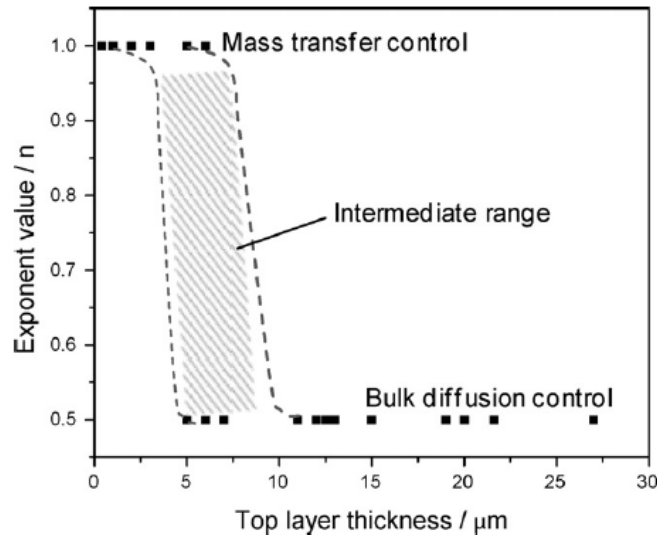


Figure 2.12 The change of n value according to the permeation control steps and the membrane thickness at temperatures between 623-773 K. Reproduced from Yun and Oyama (2011); with permission of Elsevier

The value of n changes between 0.5 and 1 according to the rate-determining steps (Steps 1 to 7 shown in Figure 2.11). In Sieverts' law, the rate-determining step is the dissolution of hydrogen atom into the bulk metal (Step 3). The rate of diffusion changes with the concentration of hydrogen atoms on the opposite sides of the metal surface, and the concentration of hydrogen changes with the square root of the pressure of hydrogen. In the modified Sieverts' law, the rate-determining step can be determined according to the types of mass transport, which are the external diffusion to Pd surface (Step 1), the external diffusion from Pd surface (Step 7), adsorption (Step 2), and desorption (Step 6). In these processes, the value of n depends linearly on the concentration of hydrogen molecule, thus the value is equal to 1 (Yun and Oyama, 2011). A more detailed explanation for finding the value of n can be found in the study by Yun and Oyama (2011). In addition, Caravella et al. (2020) emphasized that if the value of n is higher than 0.5, this can be explained with either the effect of surface phenomena or the thickness of the membrane. The operating conditions (temperature and pressure) and the properties of geometry (thickness of layers, porosity, the size of the pore) can affect the value of n . In addition, in the case of supported Pd-based membranes constituted of a thin Pd-based layer deposited on a porous support, the permeation of hydrogen may be described by different mechanisms besides the solution-diffusion such as Knudsen diffusion, surface diffusion, ordinary diffusion, and viscous flow. A more detailed explanation on the change of n values with the operating conditions can be found in the study of Bellini et al. (2010).

In most cases, the H_2 perm-selectivity is reported with finite values, and this may be due to the not uniformity of the dense separative layer and the consequent presence of defects. In the intermediate interval of ' n ' values from 0.5 to 0.8, the transport of other gases may take place with a Knudsen diffusion mechanism or a viscous flow, whereas H_2 permeation is regulated by the solution/diffusion associated with other contributions given by the Knudsen mechanism and viscous flow. In Eq. (2.50), each aforementioned mechanism contributing to the total flux of H_2 permeating through the membrane is taken into account.

$$J_{H_2}^{Total} = \frac{1}{\frac{1}{J_{H_2}^{SD}} + \frac{1}{J_{H_2}^K} + \frac{1}{J_{H_2}^{HP}}} \quad (2.50)$$

$J_{H_2}^{SD}$ represents the term indicating the contribution of solution/diffusion mechanism, expressed by Eq. (2.48), whereas the Knudsen and viscous flow represent the other two contributions expressed by Eqs. (2.51) and (2.52).

$$J_{H_2}^K = \frac{\varepsilon d_p}{\tau L} \left(\frac{8}{9\pi MRT} \right)^{1/2} \Delta p_{H_2} \quad (2.51)$$

$$J_{H_2}^{HP} = \frac{r^2}{8\eta L P_0} P_{AVE} \Delta p_{H_2} \quad (2.52)$$

where ε is the membrane porosity, d_p is the pore diameter, τ is the tortuosity, L is the thickness, M is the molecular weight of diffusing gas, Δp_{H_2} is the transmembrane hydrogen partial pressure, η is the viscosity, P_{AVE} is the average pressure, P_0 is the outlet pressure, and r is the radius.

2.6.2 Modeling of Each Hydrogen Permeation Step

To investigate the hydrogen permeation behavior through the membrane accurately, non-ideal transport phenomena in different membrane layers should be considered in the modeling. With the use of such models, a more thorough understanding of the behavior of the permeation with the change of operating (pressure, temperature) and geometric (membrane thickness) parameters can be achieved. Figure 2.13 shows the schematic of the processes and transport resistances for hydrogen permeation through a supported membrane. As you can see from this figure, the reaction and permeation sides are the annulus and tube sides, respectively. The chemical reactions in the reaction side for hydrogen production occur through the z-direction, whereas the produced hydrogen (hydrogen flux) passes from the reaction to permeation sides through minus r-direction. Hydrogen permeation through the supported Pd-based membrane including Pd-layer and support material can change with the transport resistance such as the concentration polarization, intrinsic resistance, and support friction according to the different membrane layers. Therefore, in this section, different

approaches for modeling the hydrogen permeation in each layer given in Figure 2.13 are presented.

2.6.2.1 External Mass Transfer

Mass flux of hydrogen due to external mass transfer in both reaction and permeation sides can be calculated as follows (Caravella et al., 2010):

$$J_{H_2} = h \cdot (C_{H_2}^{Bulk} - C_{H_2}^{Surface}) \quad (2.53)$$

where J_{H_2} is the hydrogen permeating flux, h is the coefficient of external mass transfer and, $C_{H_2}^{Bulk}$ and $C_{H_2}^{Surface}$ are the concentration of hydrogen on the bulk metal and surface, respectively.

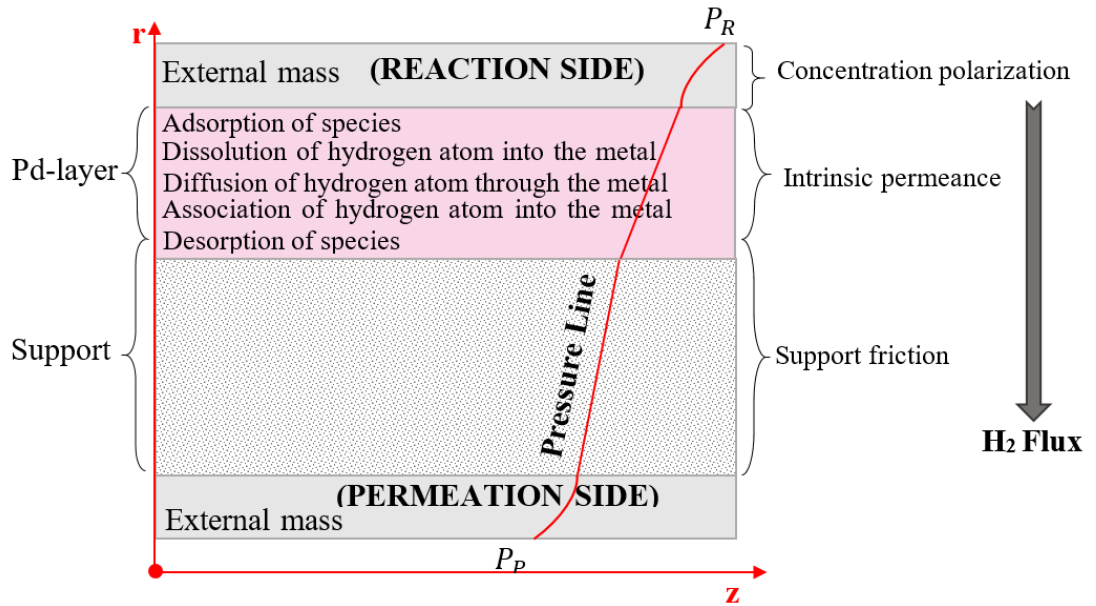


Figure 2.13 Schematic of the processes and transport resistances for hydrogen permeation through a supported membrane (Not to scale)

2.6.2.2 Modeling of Pd-layer

Caravella et al. (2010) evaluated the driving forces for each elementary step of the hydrogen permeation in a self-supported membrane. These steps are the adsorption and desorption, surface-to-bulk and bulk-to-surface, and diffusion, respectively.

2.6.2.3 Adsorption and Desorption

The hydrogen flux of adsorption (Eq. (2.54)) and desorption (Eq. (2.55)) steps are calculated as follows (Caravella et al., 2010):

$$J_{H_2}^{Ads} \cong \frac{S_0}{K\sqrt{2\pi M_{H_2} RT}} (1 - \theta_{react})^2 P_{react} - N_s^2 k_{Des}^0 \exp\left(-\frac{2E_{Des}}{RT}\right) \theta_{react}^2 \quad (2.54)$$

$$J_{H_2}^{Des} \cong N_s^2 k_{Des}^0 \exp\left(-\frac{2E_{Des}}{RT}\right) \theta_{perm}^2 - \frac{S_0}{K\sqrt{2\pi M_{H_2} RT}} (1 - \theta_{perm})^2 P_{perm} \quad (2.55)$$

where S_0 , K , N_s , and k_{Des}^0 are the sticking coefficient for a Pd-based clean surface (taken as 1), a constant (taken as 0.05), the total superficial concentration of free sites, and the pre-exponential factor of the desorption kinetic constant, respectively. θ and P are the surface coverage due to atomic hydrogen and the pressure. These subscripts, R and P, refer to reaction and permeate sides, respectively. The detailed derivation of the modeling equations for the Pd-layer can be found in the study by Caravella et al. (2008).

2.6.2.4 Dissolution (surface-to-bulk) and Association (bulk-to-surface)

The hydrogen flux of surface-to-bulk (Eq. (2.56)) and bulk-to-surface (Eq. (2.57)) steps are calculated as follows (Caravella et al. 2010):

$$J_{H_2}^{SB} \cong \frac{N_s \lambda_{j0}}{6} \left[(1 - \xi_{react}) \frac{T^{0.25}}{c_1} \exp\left(-\frac{E_{SB}}{RT}\right) \sqrt{K} \frac{\theta_{react}}{1 - \theta_{react}} - \xi_{react} \exp\left(-\frac{E_{BS}}{RT}\right) \right] \quad (2.56)$$

$$J_{H_2}^{BS} \cong \frac{N_s \lambda_{j0}}{6} \left[\xi_{perm} \exp\left(-\frac{E_{SB}}{RT}\right) - (1 - \xi_{perm}) \frac{T^{0.25}}{c_1} \exp\left(-\frac{E_{BS}}{RT}\right) \sqrt{K} \frac{\theta_{perm}}{1 - \theta_{perm}} \right] \quad (2.57)$$

where λ_{j0} , c_1 , ξ , and E are the jump frequency, a constant (taken as 10.154), the atomic hydrogen concentration in Pd bulk, and the activation energy, respectively. The detailed derivation of the modeling equations for the Pd-layer can be found in the study by Caravella et al. (2008).

2.6.2.5 Diffusion

The calculation of the diffusion of hydrogen atom through Pd-based lattice was proposed by Caravella et al. (2008). They considered the chemical potential gradient of hydrogen as the driving force of permeation. The hydrogen flux of diffusion of hydrogen atom through the Pd-based lattice is calculated as follows:

$$J_{H_2}^{Diff} = \frac{N_b}{2\delta^{Mem}} D_H^0 \exp\left(-\frac{E_{Diff}}{RT}\right) \left[(\xi_{react} - \xi_{perm}) + \left(\frac{1}{2} + \frac{b}{T}\right) (\xi_{react}^2 - \xi_{perm}^2) \right] \quad (2.58)$$

where N_b , δ^{Mem} , and D_H^0 are the total bulk concentration of free sites, the membrane thickness, and the pre-exponential factor of the atomic hydrogen diffusion coefficient, respectively. The detailed derivation of the modeling equations for Pd-layer can be found in the study of Caravella et al. (2010).

2.6.2.6 Modeling of Porous Support

The mass transport in porous support can be investigated using different modeling approaches including the advection-diffusion model, the Dusty-Gas Model, and the binary friction model. It was found that the advection-diffusion model is insufficient to define the mass transport in porous media, though mathematically it is easy (Webb, 1998). Therefore, Dusty-Gas (Mason et al., 1983) and binary friction models (Kerkhof, 1996) were more commonly used to investigate the modeling of mass transfer in porous media, which contains the molecular diffusion, Knudsen diffusion, and viscous flow.

Dusty-Gas Model

Firstly, Dusty-Gas model equations used in the studies of Caravella and his colleagues are given for both single gas and mixture gas. When the fluid on the permeation side is pure hydrogen, there is no mutual binary diffusion, and the following equation is used for the multilayer porous support (Caravella et al., 2014).

$$J^{Tot} = J_j^{Kn} + J_j^{Vs} = \frac{D_{Eff,j}^{Kn}}{RT} \frac{\Delta P_j}{\delta_j} + \frac{\frac{d_{pore}^2}{32} \frac{\epsilon_j}{\tau_j} \Delta(P_j^2)}{2RT\eta \delta_j} \quad (2.59)$$

where J is the molar flux. Subscript, j, indicates the jth layer. The superscripts, Tot, Kn, and Vs, indicate total, Knudsen, and viscous, respectively. Knudsen flux is described by a linear driving force (ΔP_j), thus, the pressure exponent is equal to one, whereas the pressure exponent for viscous flux is equal to two (Caravella et al., 2014). When the temperature increases, the viscosity, η , decreases for both Knudsen and Viscous fluxes. The viscosity of a single gas (η_i) is calculated using the following equation (Caravella et al., 2008):

$$\eta_i = \beta_1 \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega_\mu} \quad (2.60)$$

The following equation is used to analyze each layer of multilayer porous support for a gas mixture (Caravella et al., 2008).

$$\sum_{j=1}^n \frac{x_j J_i - x_i J_j}{C_{total} D_{ij, effective}^{Maxwell-Stefan}} + \frac{J_i}{C_{total} D_{i, effective}^{Knudsen}} = -\frac{x_i}{RT} \nabla_{T,P} \mu_i - \frac{x_i \bar{V}_i}{RT} \nabla P - x_i \frac{B_0}{\eta D_{i, effective}^{Knudsen}} \nabla P \quad (2.61)$$

The factor B_0 is calculated as follows:

$$B_0 = \frac{d_{pore}^2}{32} \quad (2.62)$$

When the components in a mixture are assumed as ideal gases, Eq. (2.61) can be transformed into Eq. (2.63).

$$\sum_{j=1}^n \frac{x_j J_i - x_i J_j}{C_{total} D_{ij, effective}^{Maxwell-Stefan}} + \frac{J_i}{C_{total} D_{i, effective}^{Knudsen}} = -\nabla x_i - \frac{x_i \bar{V}_i}{RT} \nabla P - x_i \frac{B_0}{\eta D_{i, effective}^{Knudsen}} \nabla P \quad (2.63)$$

Knudsen diffusivity can be calculated using the following equations:

$$D_i^{Knudsen} = 4850 \cdot d_{pore} \sqrt{\frac{T}{M_i}} \quad (2.64)$$

$$D_{i, effective}^{Knudsen} = D_i^{Knudsen} \frac{\varepsilon^{Support}}{\tau} \quad (2.65)$$

The properties of mixture gas such as binary mixture diffusivities and viscosity of a mixture can be calculated using the study of Caravella et al. (2008). More detailed explanations can be found in the studies by Caravella et al. (2008) and Caravella et al. (2014). Secondly, Li et al. (2016) compared Dusty-Gas and binary friction models. The flux of a mixture gas used in their study was given according to the isothermal conditions for the Dusty-Gas model.

$$\sum_{i=1, j \neq 1}^n \frac{x_i J_j - x_j J_i}{D_{ij}^e} - \frac{J_i}{D_{K,i}^e} = \frac{P}{RT} \nabla x_i + \left[1 + \frac{B_v P}{D_{K,i}^e \mu} \right] \frac{x_i}{RT} \nabla P \quad (2.66)$$

Significant computing resources are needed to solve this equation due to its complexity. Fortunately, in general, this equation can be much simplified for binary gas mixture, because only hydrogen can permeate through the membrane (Li et al., 2016). The following equations can be simplified for the binary gas mixture (hydrogen (A) and sweep gas (B)) according to zero-flux for sweep gas ($J_B = 0$). Components i and j are considered as hydrogen (A) and sweep gas (B) in Eq. (2.67); the opposite is for Eq. (2.68).

$$-\frac{x_B J_A}{D_{AB}^e} - \frac{J_A}{D_{K,A}^e} = \frac{P}{RT} \nabla x_A + \left[1 + \frac{B_v P}{D_{K,A}^e \mu} \right] \frac{x_A}{RT} \nabla P \quad (2.67)$$

$$\frac{x_B J_A}{D_{AB}^e} = \frac{P}{RT} \nabla x_B + \left[1 + \frac{B_v P}{D_{K,B}^e} \right] \frac{x_B}{RT} \nabla P \quad (2.68)$$

When Eqs. (2.67) and (2.68) are summed, the terms, $(x_A + x_B)$ and $(\nabla x_A + \nabla x_B)$, are taken as 1 and 0, respectively, and the term of molecular diffusivity (D_{AB}^e) is neglected, then the hydrogen flux equation is written as follows:

$$J_A = -\frac{D_{K,A}^e \nabla P}{RT} \left[\left(1 + \frac{B_v P}{D_{K,A}^e} \right) x_A + \left(1 + \frac{B_v P}{D_{K,b}^e} \right) (1 - x_A) \right] \quad (2.69)$$

More detailed explanations can be found in the study by Li et al. (2016).

Binary Friction Model

Some discrepancies in the formulation of the Dusty-Gas model were found by Kerkhof (1996) and Zhdanov (1996). They examined separately the derivation of the Dusty-Gas model found by Mason et al. (1983), and both found that the viscous term was considered twice in the model. Therefore, to eliminate the discrepancies, a binary friction model was developed by Kerkhof (1996) with fitting the gradients of pressure and molar fraction. The equation of this binary friction model is shown below. More detailed explanations can be found in the study by Li et al. (2016).

$$\sum_{i=1, j \neq 1}^n \frac{x_i J_j - x_j J_i}{D_{ij}^{e,BFM}} - \left(D_{ij}^{e,BFM} + \frac{B_v}{\kappa_i} \right)^{-1} J_i = \frac{1}{RT} \nabla P_i \quad (2.70)$$

2.6.3 Comparison of Hydrogen Permeation Models

Table 2.12 shows a summary of some of the key studies on the modeling of hydrogen permeation through the self-supported/supported membrane found in the literature. This table shows that the type of porous model mainly used in this type of modeling is the Dusty-Gas model. Most of the models include the mass transfer modeling in one or two layers; but Caravella et al. (2008) developed a model that includes transport phenomena in all layers, e.g. external mass transfer, adsorption and

desorption, dissolution and association, diffusion, and mass transport in porous support.

Table 2.12 The summary of the modeling studies of hydrogen permeation through the membrane

Ref.	Membrane Type	Mass Transfer Modeling			Type of Porous Model
		External	Pd layer	Support	
Bellini et al., 2020	Self-supported				n/a
Caravella et al., 2008	Supported				Dusty-Gas Model
Caravella et al., 2014	Supported				Dusty-Gas Model
Li et al., 2016	Supported				Dusty-Gas/ Binary Friction Models
Caravella et al., 2009	Self-supported				n/a
Vadrucci et al., 2013	Self-supported				n/a

2.7 Modeling Approaches for Membrane Reactors

MR models can be classified into three categories according to their methods as follows:

- A theoretical model is developed using the governing (mass, energy, and momentum) and auxiliary (reaction kinetics, transport, and hydrogen flux through the membrane) equations. These models are validated with the experimental data and can be used to find the effect of different operating conditions on the performance. However, significant time and computer resources are necessary to develop and solve these models (Alavi et al., 2017; Gallucci et al., 2004).
- An empirical model is developed by the fitting of the experimental data. Although these models are easily developed, they are the least beneficial (Alavi et al., 2017; Basile et al., 2015).
- A semi-empirical model can be considered as a theoretical model that calculates some parameters using the experimental data through the data fitting method (Alavi et al., 2017). These models provide to understand the system with less effort than the theoretical models.

In a MR, different phenomena occur as follows (Gallucci et al., 2011):

- Firstly, the reactants are transferred from the feed gas or fluid to the catalyst on the reaction side.

- The reactants pass through the catalyst pores and are adsorbed on the pore surfaces.
- The products from the reactions are desorbed from the pore surfaces and are transferred back into the fluid on the reaction side.
- The desired product (hydrogen) is permeated from the fluid in the reaction side to the surface of the membrane.
- Finally, hydrogen is passed through the membrane and separated from retentate gases.

The last phenomenon, hydrogen permeation through the membrane, depends on the membrane type (dense or porous, organic, or inorganic, self-supported or supported, etc.) and the different rate-determining steps in the hydrogen Solution-Diffusion mechanisms. When all the phenomena are considered, it is almost impossible or very complex to solve the modeling equations of a packed bed MR. The phenomena mentioned above can be solved and investigated independently from each other, however, there are no available data to validate them. Therefore, the model of a packed bed MR should be developed with simplifying modeling approaches covering the most critical and prominent properties of the problem (Gallucci et al., 2011). The complexity of a mathematical model of MRs depends on the following considerations:

- Energy transport (isothermal and non-isothermal)
- Spatial dimensions (1-D, 2-D, and 3-D)
- Phases involved (Pseudo-homogeneous and heterogeneous)
- Other transport mechanisms

Up to now, many studies on MR modeling have been examined according to the isothermal conditions. In the isothermal conditions, the effects of axial and radial heat transfer are neglected and it is supposed that there are no heat transfer resistances between the membrane and the wall and between the membrane and the fluid (Koukou et al., 1997). However, the temperature distribution within the MR has a significant effect on the performance of the MRs as discussed in Energy Balance Parts of Sections 2.7.1.1 and 2.7.1.2.

2.7.1 Modeling Approaches Based on Different Continuum Models

In reaction engineering application models, both continuum and discrete models can be used. However, mainly continuum models have been used in the literature to define the mass and heat transfer in the reactor. Froment and Bishoff (1990) divided models into two categories as pseudo-homogeneous and heterogeneous. In the pseudo-homogeneous model, the fluid and the particles of catalyst are supposed to have only one phase or single pseudo phase, whereas, in the heterogeneous model, the fluid and the particles of catalyst are supposed to have two phases (Alavi et al., 2017).

In the MRs, the multiphase approaches are required due to the fluid phases and porous structure. More clearly, at the reaction side, the feed gas and the catalyst providing the reactions cause the formation of both gas and solid phases, and thus the solution of the problems involving these phases are more expensive and require time. In the literature, most of the modeling studies on the packed-bed MR assume that the gas and solid phases are one equivalent phase in the quasi-homogeneous modeling approach, which is then arranged with the porosity and effective transport coefficients to distinguish gas and solid phases (Mangold et al., 2010). Nevertheless, all the balance equations, which are mass, energy, momentum, and transport of species, must be considered for each phase separately. The heterogeneous model equations for the gas and solid phases are given in Table 2.13.

In Table 2.13, ρ , h , p , and T are the density, the enthalpy, the pressure, and the temperature, respectively. y_i is the mass fraction for n species. $\bar{\tau}$, $\vec{m}_i^{Diff}$, e , c_p , $\dot{q}$, and ε are defined as stress tensor, mass flux, specific energy, specific heat capacity, heat flux, and porosity, respectively. $\vec{v}_f$ and R_i are the interstitial velocity and the reaction source term, respectively. The superscripts and subscripts, Diff, f, g, i, s, and *, are defined as the molecular diffusion, fluid, gas, component index, solid, and partial, respectively. The detailed calculations of these terms can be found in the study of Mangold et al. (2010).

Table 2.13 Heterogeneous model equations involving both gas and solid phases (Adapted from Mangold et al. (2010))

Gas Phase (Fluid zone)	Solid Phase (Porous zone)
Total mass balance $\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0$	Total mass balance $\frac{\partial(\varepsilon \rho_f)}{\partial t} + \nabla \cdot (\varepsilon \rho_f \vec{v}_f) = 0$
Momentum Balance $\frac{\partial(\rho \vec{v})}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) + \nabla \cdot p - \nabla \cdot (\vec{\tau}) - \rho \vec{g} = 0$	Momentum Balance $\frac{\partial(\varepsilon \rho_f \vec{v}_f)}{\partial t} + \nabla \cdot (\varepsilon \rho_f \vec{v}_f \vec{v}_f) + \nabla \varepsilon p - \nabla \cdot (\varepsilon \vec{\tau}) - \varepsilon \rho_f \vec{g} = \varepsilon \vec{f}$ Source term: $\vec{f} = f_1 \vec{v}_f + f_2 \mid v_f \mid \vec{v}_f$
Transport of species $\frac{\partial(\rho x_i)}{\partial t} + \nabla \cdot (\rho \vec{v} x_i) + \nabla \cdot \vec{m}_i^{Diff} = 0$ If $\rho \vec{v}$ is taken as constant: $\rho \frac{\partial(x_i)}{\partial t} + \rho \vec{v} \nabla \cdot (x_i) + \nabla \cdot \vec{m}_i^{Diff} = 0$	Transport of species $\frac{\partial(\varepsilon \rho_f x_i)}{\partial t} + \nabla \cdot (\varepsilon \rho_f \vec{v}_f x_i) + \nabla \cdot \vec{m}_i^{Diff} = R_i$
Energy Balance $\frac{\partial(\rho e)}{\partial t} + \nabla \cdot [\vec{v}(\rho e + p)] + \nabla \cdot (\dot{q} + \sum_{i=1}^N h_i \vec{m}_i^{Diff}) - \nabla(\vec{\tau} \cdot \vec{v}) = 0$ $e = h - \frac{p}{\rho} + \frac{v^2}{2}; h = \sum_{i=1}^n y_i h_i; h_i = \int_{T_{ref}}^T c_{p,i} dT$ If $\rho \vec{v}$ and c_p are taken as constant: $c_p \rho \frac{\partial T}{\partial t} + c_p \rho \vec{v} \nabla T + \nabla \cdot (\dot{q} + \sum_{i=1}^N h_i \vec{m}_i^{Diff}) - \frac{\partial p}{\partial t} - \vec{v} \nabla p - \nabla(\vec{\tau} \cdot \vec{v}) = 0$	Energy Balance $\frac{\partial}{\partial t}(\varepsilon \rho_f e_f + (1 - \varepsilon) \rho_s e_s) + \nabla \cdot [\varepsilon \vec{v}_f(\rho_f e_f + p)] + \nabla \cdot (\dot{q} + \sum_{i=1}^N h_i \vec{m}_i^{Diff}) - \nabla(\varepsilon \vec{\tau} \vec{v}_f) = \sum_{i=1}^n \frac{\tilde{h}_i^0 R_i}{\tilde{M}_i}$

Different continuum models for MRs in the literature are summarized according to their dimensions and balance equations in Table 2.14. In all the studies shown in Table 2.14, the momentum balance equation in the permeation side was neglected, and the mass balance equation in the reaction side was included. According to the literature survey, 1-D models are generally examined according to the pseudo-homogeneous approach, whereas 2-D models are examined according to the heterogeneous approach. For example, Cruz and Silva (2017) investigated temperature profiles of gas and solid phases in both conventional fixed bed reactor and fixed bed MR and the results for the fixed bed MR are given in Figure 2.14. A detailed explanation is found in the study of Cruz and Silva (2017).

Table 2.14 Different continuum membrane reactor models found in the literature

Model Approach	Dimension	Ref.	Balance Equations					
			Mass		Energy		Momentum	
			R	P	R	P	R	P
Pseudo-homogeneous	1-D	(Mendes et al., 2011)						
		(Leonzio,2016)						
		(Alavi et al., 2017)						
		(Leonzio, 2019)						
	2-D	(Kyriakides et al., 2016)						
Heterogeneous	1-D	(Pedernera et al., 2007)						
		(Pantoleonos et al., 2012)						
		(Taji et al., 2018)						
	2-D	(Ghouse and Adams, 2013)						
		(Cruz and Silva, 2017)						
		(Kuncharam and Dixon, 2020)						

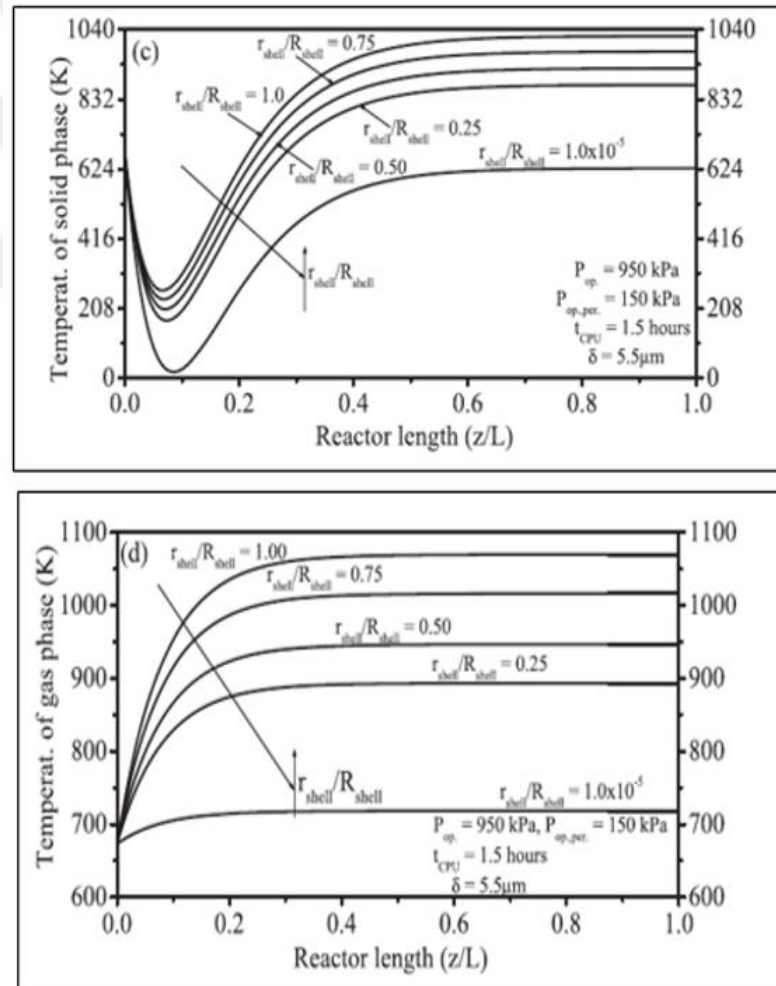


Figure 2.14 Temperature profiles at the solid surface of the gas phase for the hot start-up simulation along the reactor length (z/L) of conventional fixed bed membrane reactor. Reproduced from Cruz and Silva (2017), with permission from Elsevier.

2.7.2 Modeling Approaches Based on Spatial Dimensions

In the literature, three different methods are found for modeling MRs according to the spatial dimensions, which are one-dimensional, two-dimensional, and three-dimensional models. One-dimensional (1-D) modeling of the MR is the most common type of modeling. In this modeling type, the property changes in only one dimension (axial coordinate) are taken into account; therefore, the solution of one-dimensional models is relatively easier than the others. However, the gradients of the concentration and the temperature in the radial coordinate significantly affect the hydrogen flux through membrane and heat transfer (Alavi et al., 2017). Therefore, a two-dimensional (2-D) modeling method that also includes the radial coordinate may be preferred. In a three-dimensional (3-D) modeling method, which gives more realistic results, the model is solved according to the 3-D geometrical representation of the MR also including the angular coordinate.

Generally, different dimensional models (1-D, 2-D, and 3-D) of MRs can be developed using the governing (mass, energy, and momentum) and the auxiliary (reaction kinetics, transport, and hydrogen flux through the membrane) equations. Mass transport equations consist of the dispersion and the permeation through the membrane of different reactants and products by chemical reactions. Mass balance equations are required to examine the distribution of concentration of each species through the reactor. When the mass balances for reaction and permeation sides are applied for a control volume, the main components of the mass balance equation are the formation and depletion rates of i species through control volume and the rate of hydrogen permeation through the membrane in control volume (Alavi et al., 2017). Energy transport equations consist of the conduction and convection between permeate and retentate gases or between the inside of the reactor and its wall, and the heat produced from the chemical reactions. Energy balance equations are required to examine the thermal performance of the reactors operating at non-isothermal conditions. Momentum transport equations consist of the pressure drops, the permeability of bed and inertial losses, viscous and drag forces, and the volumetric forces on the fluid. In addition, the kinetic reaction rate expressions for the chemical

reactions that produce hydrogen from methane should be chosen according to the appropriate catalyst type. In addition, the equation of the hydrogen flux through the membrane should be chosen according to the appropriate membrane type.

2.7.2.1 One-Dimensional Model

Figure 2.15 shows the schematic of the geometry of a tubular MR considered in the 1-D modeling approach. For the selected configuration, the annulus side is the permeation side collecting the hydrogen produced from the reaction side; whereas the tube side is the reaction side in which the chemical reactions occur to produce hydrogen from methane. In this subsection, all governing equations (mass, energy, and momentum) used in the 1-D modeling of a MR are given in detail according to the different studies found in the literature.

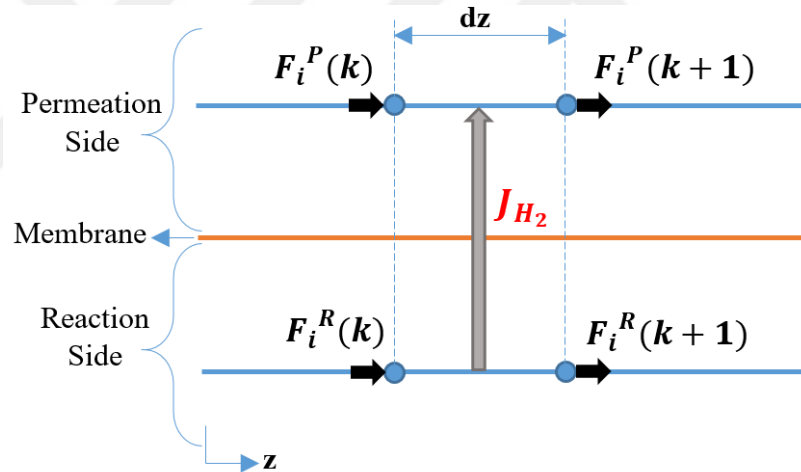


Figure 2.15 The schematic of the geometry of a tubular MR considered in the 1-D modeling approach

➤ Mass Balance

Mass transport equations in the MR include the dispersion and the permeation through the membrane of the products and reactants at the chemical reactions. In the literature, the dispersion term of the mass balance equations is neglected in most of the 1-D modeling studies such as Alavi et al. (2017), Patel and Sunol (2007), Oyama and Hacırlıoğlu (2009), and Bruni et al. (2019). For example, Patel and Sunol (2007) studied the modeling and simulation of a MR including burner, reformer, and sweep

gas sides, which produces hydrogen from methane. The dispersion term was ignored in this study and the mass balance equations for reaction (Eqs. (2.71) and (2.72)) and permeation (Eq. (2.73)) sides were given as follows:

$$-\frac{d}{dz}(\varepsilon u_r C_{r,i}) + \rho_r r_{r,i} = 0 \quad (\text{for all components except hydrogen}) \quad (2.71)$$

$$-\frac{d}{dz}(\varepsilon u_r C_{r,i}) + \rho_r r_{r,i} - S_m J \left(\frac{t_m}{t_r} \right) = 0 \quad (\text{for hydrogen}) \quad (2.72)$$

$$-\frac{d}{dz}(u_m C_{m,i}) + S_m J \quad (\text{for hydrogen}) \quad (2.73)$$

where ε , u , C , ρ , S_m , J , and t are the reformer bed porosity, velocity, concentration, density, hydrogen permeation area per unit volume of sweep gas channel, hydrogen permeation, and thickness, respectively. The subscripts, r, i, and m, represent reformer, i^{th} reactant, and sweep gas, respectively. In the study of Patel and Sunol (2007), when the reactor length (z) was taken as 0, the boundary conditions, the concentration of reformer ($C_{r,i}$), and the concentration of sweep gas ($C_{m,i}$), were taken as $C_{r,i} = C_{r,i}(0)$ and $C_{m,i} = C_{m,i}(0)$, respectively.

In another study, Oyama and Hacırlıoğlu (2009) conducted an experimental study for steam methane reforming reaction occurring in both CR and MR at different pressures (1-20 atm) and temperatures (873-923 K). At the same time, this study focused on the comparison of 1-D and 2-D analyses using the experimental data. Alavi et al. (2017) developed a 1-D model of a MR in which the reaction side is the shell side, and the permeation side is the tube side. In these studies, similar mass balance equations were used. Mass balance equations for reaction (Eqs. (2.74) and (2.75)) and permeation (Eqs. (2.76) and (2.77)) sides were given as follows:

$$\frac{dF_{i,r}}{dz} = \rho_b A_c \sum_i^{N_s} v_{i,j} r_j \quad (\text{for } i=\text{all components except for hydrogen}) \quad (2.74)$$

$$\frac{dF_{i,r}}{dz} = \rho_b A_c \sum_i^{N_s} v_{i,j} r_j - J_{H_2} P_M \quad (\text{for } i=\text{hydrogen}) \quad (2.75)$$

$$\frac{dF_{i,p}}{dz} = J_{H_2} P_M \quad (\text{for } i=\text{hydrogen}) \quad (2.76)$$

$$\frac{dF_{i,p}}{dz} = 0 \text{ (for i=sweep gas)} \quad (2.77)$$

where F_i , ρ_b , A_c , J_{H_2} , $v_{i,j}$, and P_M are the molar flux of species, the bed density, the cross-sectional area of reaction side, the hydrogen permeation flux, the stoichiometric coefficient of component i in the reaction j, and the perimeter of the membrane ($2\pi r$), respectively.

In some studies found in the literature, the dispersion term in the mass balance equations was taken into account. For example, Mendes et al. (2011) developed a 1-D model of a MR considering the axial dispersion. Mass balance equations in the reaction side were written according to the partial mass balances (Eq. (2.78)) and total (Eq. (2.79)). The partial balance equation includes only single species (i); whereas the total balance equation includes all species.

$$\frac{d}{dz}(u_r P_{i,r}) - \frac{d}{dz}\left(D_{ax} P_r \frac{d}{dz}\left(\frac{P_{i,r}}{P_r}\right)\right) + \frac{2\pi r_m}{\varepsilon_b A_r} RT J_i - \frac{W_{cat}}{\varepsilon_b V_r} RT v_i r = 0 \quad (2.78)$$

$$\frac{d}{dz}(u_r P_r) + \frac{2\pi r_m}{\varepsilon_b A_r} RT \sum_i J_i - \frac{W_{cat}}{\varepsilon_b V_r} \sum_i v_i r = 0 \quad (2.79)$$

Mass balance equations in the permeation side were written according to the partial mass balances (Eq. (2.80)) and total (Eq. (2.81)) (Mendes et al., 2011).

$$\frac{d}{dz}(u_p P_{i,p}) + f \frac{2\pi r_m}{A_p} RT J_i = 0 \quad (2.80)$$

$$P_p \frac{du_p}{dz} + f \frac{2\pi r_m}{A_p} RT \sum_i J_i = 0 \quad (2.81)$$

where u , P_i , P , D_{ax} , r_m , A , J , W_{cat} , V_r , v_i , and r are the velocity, the partial pressure of component i, the total pressure, the effective axial dispersion coefficient, the internal radius of the membrane, the cross-sectional area of reaction side, the flux through the membrane, the mass of catalyst bed, the volume of reaction side, the stoichiometric coefficient and the reaction rate, respectively. The term, f , can be -1 or +1 according to the flow type (co-current/counter-current flows). The r and p subscripts denote the

reaction and permeation sides. The boundary conditions used for solving the mass balance equations are given in Table 2.15.

Table 2.15 Boundary conditions for the reaction and permeation sides used in the mass balance equations for the counter-current flow type (Mendes et al., 2011)

Reactor Length	Reaction Side	Permeation Side (Counter-current mode)
$z=0$	$\frac{d}{dz} \left(\frac{P_{i,r}}{P_r} \right) = - \frac{u_r}{\varepsilon_b D_{ax}} \left(\frac{P_{i,r}(in) - P_{i,r}}{P_r} \right)$ $u_r = u_r(in) = \frac{u_f}{\varepsilon_b}$ $P_r = P_r(in) = P_f$	$u_p = 0$ $P_{i,p} = P_p$
$z=L$	$\frac{d}{dz} \left(\frac{P_{i,r}}{P_r} \right) = 0$	$P_{i,p} = P_{i,p}(in)$ $u_p = u_{i,p}(in)$

When the literature studies mentioned above are examined, the mass balance equations used in the MRs have been mostly written for transient conditions (Eqs. (2.82) and (2.83)). In general, the mass balance equations used in the 1-D modeling studies in the literature are given as follows according to the reaction (Eq. (2.82)) and permeation (Eq. (2.83)) sides:

- For Reaction Side:

$$\frac{1}{RT_R} \frac{\partial P_i^R}{\partial t} = \left[\frac{1}{RT_R} D_i \frac{\partial^2 P_i^R}{\partial z^2} \right] - \left[\frac{\partial F_i^R}{\partial z} \right] + \left[\sum_{j=1}^{N_R} \nu_{i,j} r_j \right] - \left[\frac{A_M}{V_R} J_i^P \right] \quad (2.82)$$

- For Permeation Side:

$$\frac{1}{RT_P} \frac{\partial P_i^P}{\partial t} = \left[\frac{1}{RT_P} D_i \frac{\partial^2 P_i^P}{\partial z^2} \right] - \left[\frac{\partial F_i^P}{\partial z} \right] + \left[\frac{A_M}{V_P} J_i^P \right] \quad (2.83)$$

where the term, $\left[\frac{1}{RT} \frac{\partial P_i}{\partial t} \right]$, is the accumulation term (the value is zero at the steady-state conditions.). The term, $\left[\frac{1}{RT} D_i \frac{\partial^2 P_i}{\partial z^2} \right]$, is the axial dispersion term applied at the second-order model and when the Peclet number is less than 1, this term will be zero. The

term, $\left[\frac{\partial F_i}{\partial z}\right]$, is the change of the molar flux of species i through the reactor length. The term, $\left[\sum_{j=1}^{N_R} \nu_{i,j} r_j\right]$, is the reaction term that occurred from the chemical reactions given in Section 2.5. The term, $\left[\frac{A_M}{V} J_i^P\right]$, is the permeation term of species i through the membrane. The permeation term (J_i^P) is given in Eqs. (2.82) and (2.83) can be positive or negative depending on the permeation and reaction sides, this term is positive for the permeation side, while is negative for the reaction side. In general, the initial and boundary conditions used in these mass balance equations for the reaction and permeation sides are given in Table 2.16.

Table 2.16 Initial and boundary conditions for the reaction and permeation sides used in the mass balance equations (Alavi et al., 2017)

Conditions	Reaction Side	Permeation Side
Initial Conditions	$P_i^R \big _{t=0} = P_i^{R,initial}$	$P_i^P \big _{t=0} = P_i^{P,initial}$
	$X_i^R \big _{t=0} = X_i^{R,initial}$	$X_i^P \big _{t=0} = X_i^{P,initial}$
Boundary Conditions	$P_i^R \big _{z=0} = P_i^{feed}$	$P_i^P \big _{z=0} = P_i^{sweep}$ (Co-current flow)
		$P_i^P \big _{z=L} = P_i^{sweep}$ (Counter flow)
	$\frac{\partial P_i^R}{\partial z} \big _{z=L} = 0$	$\frac{\partial P_i^P}{\partial z} \big _{z=L} = 0$ (Co-current flow)
		$\frac{\partial P_i^P}{\partial z} \big _{z=0} = 0$ (Counter flow)

➤ Energy Balance

Energy balance equations are required to examine the thermal performance of the reactors operating at non-isothermal conditions. In the lab-scale MRs, isothermal conditions can be assumed; however, in the large-scale commercial applications, the temperature changes within the MRs are generally not negligible. When the temperature of fluids in the reaction side changes with the reactor length, the reaction rates are used in the calculation, and thus the amount of produced and consumed species changes. For cases where the temperature changes within the reactor are considered, the energy balance and mass balance equations should be simultaneously solved to examine the distributions of temperature and concentration.

In the literature, generally, isothermal and isobaric conditions are assumed in the permeation side, since no chemical reactions take place on this side, and there is almost no other gas except hydrogen and sweep gas. Therefore, the temperature, especially at the reaction side, affects the constants used in the reaction rate expressions (given in Section 2.5) and thus the mass balance equations on the reaction side. For example, for the reaction side, the temperature equation (Eq. (2.84)) including the reaction heat, the advection heat transport, and the overall heat transfer between the heater and the reaction side was considered in the modeling of MR in the study by Fernandes and Soares (2006).

$$\frac{d\langle T \rangle_A}{dz} = \frac{\frac{2\pi r_{i,o}}{\pi(r_{o,i}^2 - r_{i,o}^2)} U_o (T_{amb} - \langle T \rangle_A) + \sum_k \langle r_k \rangle_A [-\Delta \langle H_k \rangle_A]}{\langle c_p \rangle_A \langle \rho \rangle_A \langle v \rangle_A} \quad (2.84)$$

where $r_{o,i}$, and $r_{i,o}$ are the external tube inner radius and internal tube outer radius, respectively. U_o , T_{amb} , r_k , ΔH_k , c_p , ρ , and v are defined as the overall heat transfer coefficient in the outer tube, the ambient temperature, the reaction rate of reaction k , the heat of reaction k , the heat capacity, the density, and the velocity, respectively. This symbol $\langle \cdot \rangle_A$ represents the area averaging operator.

In the literature, some studies investigated the non-isothermal conditions in both the separation and the reaction sides. For example, Marigliano et al. (2001) used the energy balance equations for the reaction (annulus) and permeation (tube) sides given in Eqs. (2.85) and (2.86), respectively.

$$\sum_{i=1}^{N_s} F_i C p_i \frac{dT_{reac}}{dz} = \frac{U_1 A_{an}}{V_{an}} (T_{oven} - T_{reac}) - \frac{U_2 A_{memb}}{V_{an}} (T_{reac} - T_{perm}) + \psi + \phi \frac{A_{memb}}{V_{an}} \quad (2.85)$$

$$\sum_{i=1}^{N_s} F_i C p_i \frac{dT_{perm}}{dz} = \frac{U_2 A_{memb}}{V_{an}} (T_{reac} - T_{perm}) + \psi + \phi \frac{A_{memb}}{V_{tube}} \quad (2.86)$$

When the studies mentioned above are examined, the energy balance equations used in the MRs are generally written for transient conditions for the reaction (Eq. (2.87)) and the permeation (Eq. (2.88)) sides as follows:

- For Tube Side:

$$\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{tube}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C p_i \frac{\partial T_{tube}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{tube}}{\partial z^2} \right] + \left[\frac{U_{MA} A_M}{V_{tube}} (T_{an} - T_{tube}) \right] + \psi + \phi \frac{A_M}{V_{tube}} \quad (2.87)$$

- For Annulus Side:

$$\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{an}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C p_i \frac{\partial T_{an}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{an}}{\partial z^2} \right] + \left[\frac{U_{an} A_{an}}{V_{an}} (T_{oven} - T_{an}) \right] - \left[\frac{U_{MA} A_M}{V_{an}} (T_{an} - T_{tube}) \right] + \psi + \phi \frac{A_M}{V_{an}} \quad (2.88)$$

where C_i , $C p_i$, U , and k_z are the molar concentration, the specific heat capacity, the overall heat transfer coefficient, and the thermal conductivity, respectively. The term, $\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{an}}{\partial t}$, is the enthalpy accumulation (the value is zero at the steady-state conditions.). The term, ψ , is defined as the heat generated by chemical reaction, and this value for the reaction side is calculated as $\sum_{j=1}^{N_{reac}} r_j (-\Delta H_j)$, whereas this value for the permeation side is zero. The term, ϕ , is defined as the temperature variation because of the enthalpy flux associated with hydrogen permeation, and this value for the reaction side is zero, whereas this value for the permeation side is calculated as $J_{H_2, perm} = h_{H_2}^{T_{reac}} - h_{H_2}^{T_{perm}}$. According to Figure 2.15, the reaction side is the tube side, while the permeation side is the annulus side. Consequently, Eq. (2.87) is used to solve the temperature distribution of the reaction side, and the term, ϕ , is neglected for the reaction side. Eq. (2.88) is used to solve the temperature distribution of the permeation side, and the term, ψ , is neglected for the permeation side. In general, the initial and boundary conditions used in these energy balance equations for the reaction and permeation sides are given in Table 2.17.

Table 2.17 Initial and boundary conditions for the reaction and permeation sides used in the energy balance equations (Alavi et al., 2017)

Conditions	Reaction Side (Tube Side)	Permeation Side (Annulus Side)
Initial Conditions	$T_{tube} \big _{t=0} = T_{tube,initial}$	$T_{an} \big _{t=0} = T_{an,initial}$
Boundary Conditions	$T_{tube} \big _{z=0} = T_{feed}$	$T_{an} \big _{z=0} = T_{sweep}$ (Co-current flow)
		$T_{an} \big _{z=L} = T_{sweep}$ (Counter flow)
	$\frac{\partial T_{tube}}{\partial z} \big _{z=L} = 0$	$\frac{\partial T_{an}}{\partial z} \big _{z=L} = 0$ (Co-current flow) $\frac{\partial T_{an}}{\partial z} \big _{z=0} = 0$ (Counter flow)

Heat transfer mechanisms (conduction and convection) are considered to calculate the overall heat transfer coefficients of both sides in the MR. The overall heat transfer coefficient depends on the thermal resistances of the materials of tube and membrane, and gas films. Alavi et al. (2017) proposed the schematic of the resistances in the MR (Figure 2.16) to find the overall heat transfer coefficient.

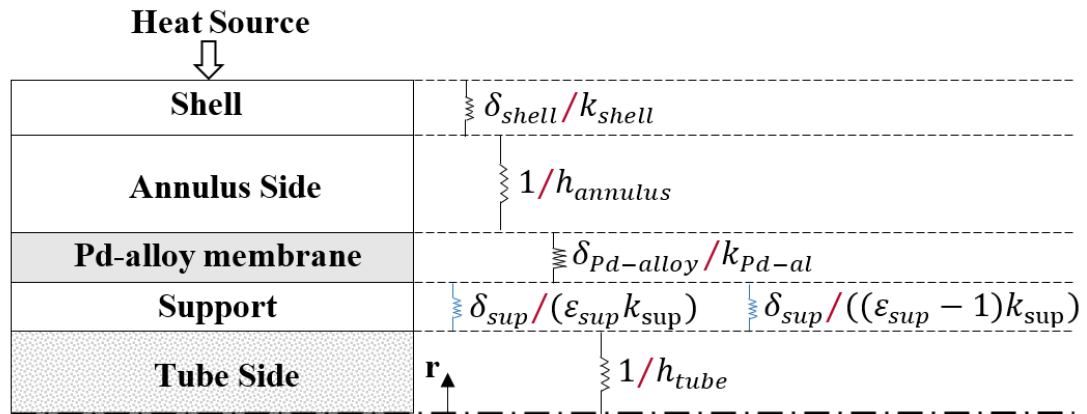


Figure 2.16 The resistances in the tubular membrane reactor

In the literature, different approaches related to the calculation of the overall heat transfer coefficient ($U, \frac{kJ}{m^2 hK}$) are found. In general, the overall heat transfer expression by Dixon (1996) was used in most of the modeling studies such as Alavi et al. (2017) and Castillo et al. (2015). This equation is given as follows:

$$U = \left[\frac{1}{\alpha_w} + \frac{1}{3} \frac{R_{ext}}{\lambda_{er}} \left(\frac{Bi+3}{Bi+4} \right) \right]^{-1} \quad (2.89)$$

where the term, λ_{er} , is the effective radial thermal conductivity of the bed. The term, α_w , is the heat transport coefficient. The term, R_{ext} , is the outer tube radius. Bi is the Biot Number and is calculated as $Bi = \alpha_w R_{ext} / \lambda_{er}$.

In another study, Beek (1962) proposed the following equation to solve the overall heat transfer coefficient.

$$U = 0.4 \frac{\lambda_g}{d_p} (2.58 \cdot Re^{1/3} \cdot Pr^{1/3} + 0.094 \cdot Re^{0.8} \cdot Pr^{0.4}) \quad (2.90)$$

where λ_g and d_p are the thermal conductivity of gas and the diameter of catalyst particles, respectively. The term, Re, is the Reynolds number and is calculated as $Re = \frac{\rho_g V_g A}{\mu_g}$. The term, Pr, is the Prandtl number and calculated as $Pr = \frac{\mu_g c_p}{\lambda_g}$. In the study of De Falco et al. (2007), the physical meaning of the overall heat transfer coefficients given in Eqs. (2.89) and (2.90) were explained in detail.

➤ *Momentum Balance*

Momentum transport consists of the pressure drops, the permeability of bed and inertial losses, viscous and drag forces, and the volumetric forces on the fluid. Momentum balance equations are required since the flow rates show differences in the small diameters due to the non-ideal flow and the permeation through the membrane. However, many studies neglected this transport in their studies, e.g. Castillo et al. (2015), Adrover et al. (2010), and Di Marcoberardino et al. (2015).

The momentum balance equations are generally solved using Ergun's equation (1952). For example, the equation for momentum balance used by Alavi et al. (2017) and Patel and Sunol (2007) is given as follows:

$$\frac{dP_r}{dz} + u_r \rho_r \frac{du_r}{dz} = -f \quad (2.91)$$

where P_r , u_r , and ρ_r are the pressure, the velocity, and the density of the reformer, respectively. The term, f , the local frictional pressure drop, can be solved using the Ergun equation (1952) given in Eq. (2.92).

$$f = -150 \frac{(1-\varepsilon)^2}{\varepsilon d_p^2} u_r \mu_r + 1.75 \frac{(1-\varepsilon) \rho_r u_r^2}{\varepsilon d_p} \quad (2.92)$$

where ε , d_p , and μ_r are the bed porosity, the hydraulic diameter of catalyst, and dynamic viscosity of the gas mixture, respectively.

In addition, with a similar approach, De Falco et al. (2007) used the following equations to solve the pressure drops through the reactor length:

$$\frac{dP}{dz} = -10^{-3} \cdot f \cdot G \cdot \frac{\mu}{\rho_{mix} d_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} \quad (2.93)$$

f can be solved using the Ergun equation (1952) given in Eq. (2.94).

$$f = 150 + 1.75 \frac{Re_p}{1-\varepsilon} \quad (2.94)$$

where Re_p is calculated as $Re_p = \frac{G \cdot d_p}{\mu}$.

➤ Comparison of 1-D Membrane Reactor Models

Table 2.18 shows the summary of the 1-D MR modeling studies for hydrogen production from methane in the literature. In all the studies shown in Table 2.18, the models were developed under the steady-state condition. Generally, the momentum balance equations were neglected, however, for the models that include this balance, it was added to the reaction side.

Table 2.18 The summary of 1-D membrane reactor modeling studies found in the literature

Ref.	Flow Type	Reaction Side	Balance Equations						Validation
			Mass		Energy		Momentum		
			R	P	R	P	R	P	
(Leonzio, 2016)	Co-current	Shell							Experimental and Theoretical
(Alavi et al., 2017)	Co-current	Shell							Theoretical
(Leonzio, 2019)	Co-current	Shell							Theoretical
(Patel and Sunol, 2007)	Co-current	Shell							None
(Bruni et al., 2019)	Co-current	Tube							Theoretical
(Marigliano et al., 2001)	Co-current	Tube and Shell							None
(De Falco et al., 2007)	Co-current	Shell							Theoretical
(Di Marcoberardino et al., 2015)	Co-current and counter-current	Shell							Experimental and Theoretical
(Solvik and Jakobsen, 2017)	Co-current	Shell							Theoretical
(Nordio et al., 2019)	Counter-current	Shell							Experimental

In recent years, most of the 1-D modeling studies on membrane reactors used for hydrogen production from steam methane reforming have examined the comparison of different reactor types. For example, Bruni et al. (2019) investigated the energy efficiency of two different membrane-based processes. One of them is a two-step process based on a steam reformer (at high temperature) and a membrane reactor for water-gas shift reaction; whereas the other is a simple packed-bed membrane reactor. Both two processes presented an increase in hydrogen production and energy efficiency with increasing pressure and steam-to-carbon ratio; however, it was found that when the space velocity increases, the performance of MR decreases. This study showed that the performance of the two-step process is better than MR, and the maximum energy efficiency is between 30% and 40%. Franchi et al. (2020) investigated numerically the steam reformer (SR), the membrane reactor (MR), and the reformer and membrane module (RMM). 1-D models including mass, energy, and momentum equations were developed. Methane conversion, temperature and pressure profiles, and carbon dioxide yield were examined and compared for these three

configurations. The results showed that when the reaction and separation sections are decoupled such as RMM, the overall conversion of methane is increased by nearly 30%, which in turn improves the system efficiency. De Medeiros et al. (2020) conducted a modelling and simulation study to evaluate the thermochemical performance analysis of Fixed Bed Reformer (FBR) and Packed-Bed Membrane Reformer (PBMR). The developed models were validated with experimental data. When the effects of the endothermic reaction temperature (ERT) on the methane conversion and hydrogen production were investigated, it was found that an increase of this parameter provides an increase in the methane conversion and hydrogen yield. When FBR and PBMR were compared, the ERT for PBMR was found to be lower than FBR due to the continuous hydrogen removal through the membrane.

2.7.2.2 Two-Dimensional Model

The 2-D model of a MR includes the mass and heat transfer considerations in the radial and axial directions, and thus this model provides more realistic results compared to a 1-D model. Figure 2.17 shows the geometry of a tubular MR used in the two-dimensional modeling approach. The annulus side is the permeation side collecting the hydrogen produced from the reaction side; whereas the tube side is the reaction side in which the chemical reactions occur to produce hydrogen from methane.

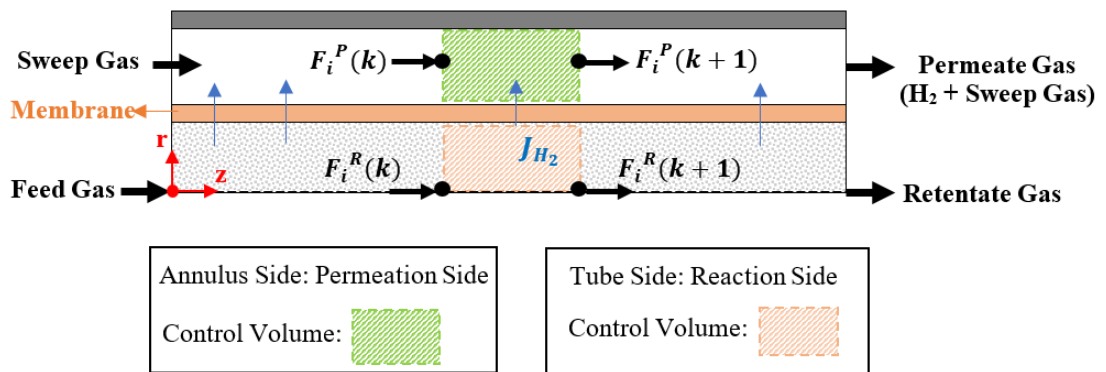


Figure 2.17 The geometry of a tubular MR used in the two-dimensional modeling approach

➤ *Mass Balance*

When the 2-D modeling studies in the literature have been examined, it has been seen that the reaction side is generally modeled as 2-D, whereas the permeation side is generally modeled as 1-D. For example, Kyriakides et al. (2013) developed a 2-D non-linear and pseudo-homogeneous mathematical model of a MR for the reaction side (Eq. (2.95)) and the permeation side (Eq. (2.96)) was considered as 1-D.

$$\frac{\partial(uC_i)}{\partial z} = \frac{\varepsilon D_{er}}{u} \left(\frac{1}{r} \frac{\partial(uC_i)}{\partial r} + \frac{\partial^2(uC_i)}{\partial r^2} \right) + \rho_b \sum_j r_j v_{i,j} \quad (2.95)$$

$$\frac{\partial(u_p C_{H_2,p})}{\partial z} = \frac{2}{r_i} \left(\frac{\varphi \cdot \exp\left(-\frac{15,700}{RT_m}\right)}{d_m} \right) (P_{H_2,r}^{0.5} - P_{H_2,p}^{0.5}) \quad (2.96)$$

where u , C , ε , D_{er} , and ρ_b are the velocity, the concentration, the void fraction of catalyst (0.85), the effective radial diffusivity ($1.238 \cdot 10^{-5} \text{ m}^2/\text{s}$), and the density of catalytic bed (1.6 kg/m^3), respectively. r_i , φ , R , T_m , and d_m are the membrane radius, the pre-exponential factor of membrane permeation ($0.00022 \text{ mol/atm}^{0.5} \cdot \text{m} \cdot \text{s}$), the universal gas constant, the temperature of the membrane, and the thickness of the membrane ($5 \cdot 10^{-4} \text{ m}$), respectively. Table 2.19 shows the boundary conditions in the mass balance equations used in the study of Kyriakides et al. (2013).

Table 2.19 Boundary conditions used in the mass balance (2013)

Boundary	Reaction and Permeation Sides
$z = 0, \forall r$	$(uC_i) = (uC_i)_{in} : (u_p C_{i,p}) = 0$
$r = r_i, \forall z$	$\frac{\partial(uC_i)}{\partial r} = 0 : \frac{\partial(uC_{H_2})}{\partial r} = \frac{J_{H_2}}{d_p P_{e_m}}$
$r = r_o, \forall z$	$\frac{\partial(uC_i)}{\partial r} = 0 : \frac{\partial(uC_{H_2})}{\partial r} = 0$

In another study, Cruz and Silva (2017), the mass balance equations were examined for the reaction (gas and solid phases) side as two-dimensional and the permeation side as 1-D. The mass balance equations for the gas phase in the reaction side are given in Eq. (2.97) (for the other gases except for hydrogen) and Eq. (2.98) (for the only hydrogen).

$$V_{g,r,shell} \frac{\partial C_{i,shell}}{\partial r_{shell}} + V_{g,z,shell} \frac{\partial C_{i,shell}}{\partial z} = 2D_{r,i,shell} \frac{\partial^2 C_{i,shell}}{\partial r_{shell}^2} + D_{z,i,shell} \frac{\partial^2 C_{i,shell}}{\partial z^2} + k_{gs,shell} \frac{(1-\epsilon)}{\epsilon} \frac{3}{R_p} (C_{p,i,shell}^{surf} - C_{i,shell}); 0 \leq z \leq L_z, 0 \leq r_{shell} \leq R_{shell} \quad (2.97)$$

$$V_{g,r,shell} \frac{\partial C_{H_2,shell}}{\partial r_{shell}} + V_{g,z,shell} \frac{\partial C_{H_2,shell}}{\partial z} = 2D_{r,H_2,shell} \frac{\partial^2 C_{H_2,shell}}{\partial r_{shell}^2} + D_{z,H_2,shell} \frac{\partial^2 C_{H_2,shell}}{\partial z^2} + k_{gs,shell} \frac{(1-\epsilon)}{\epsilon} \frac{3}{R_p} (C_{p,H_2,shell}^{surf} - C_{H_2,shell}) - \frac{\pi}{L_z} J_{H_2,shell}; 0 \leq z \leq L_z, 0 \leq r_{shell} \leq R_{shell} \quad (2.98)$$

The mass balance equation of solid phases in the reaction side is given as follows:

$$k_{gs,shell} \frac{(1-\epsilon)}{\epsilon} \frac{3}{R_p} (C_{p,i,shell}^{surf} - C_{i,shell}) = \rho_{cat,shell} \eta_{j,shell} r_{i,shell} \quad (2.99)$$

where V_g is the superficial velocity. $C_{i,shell}$, $C_{p,i,shell}^{surf}$, $D_{r,i,shell}$, and $D_{z,i,shell}$ are the concentration of component i on the shell side, the concentration of component i at the particle surface, the radial dispersion of component i on the shell side, and the axial dispersion of component i on the shell side, respectively. $k_{gs,shell}$, R_p , L_z , $J_{H_2,shell}$, $\rho_{cat,shell}$, $\eta_{j,shell}$, and $r_{i,shell}$ are the gas-solid mass transfer on the shell side, the radius of the solid particles, the reactor length, the density of catalyst on the shell side, the effectiveness factor, and the net rate of i components on the shell side, respectively.

Secondly, the mass balance equation in the permeation side is given as follows:

$$\frac{dY_{H_2,perm}}{dz} = \frac{2\pi R_m L_z}{\delta_m F_{CH_4,0}} \varphi_0 \exp\left(-\frac{E_{H_2}}{RT_{av}}\right) (P_{H_2,perm}^{0.5} - P_{H_2,shell}^{0.5}) \quad (2.100)$$

where $Y_{H_2,perm}$ is the hydrogen recovery on the permeation side. R_m , δ_m , $F_{CH_4,0}$, E_{H_2} , and T_{av} are the membrane radius, the thickness of the Pd-layer, the initial molar flow rate of methane, the activation energy of hydrogen, and the average temperature, respectively. Table 2.20 shows the inlet and boundary conditions for mass balance equations used in the study of Cruz and Silva (2017).

Table 2.20 The inlet and boundary conditions for the mass balance equations (Cruz and Silva, 2017)

Boundary	Reaction Side	Permeation Side
$z=0$	$D_{z,i,shell} \frac{\partial C_{i,shell}}{\partial z} \Big _{z=0} = k_{gs,shell} (C_{i,shell} \Big _{z=0} - C_{i,shell}^{in})$	$Y_{H_2,perm} \Big _{z=0} = 0$
$z=L_z$	$\frac{\partial C_{i,shell}}{\partial z} \Big _{z=L_z} = 0$	$\frac{dY_{H_2,perm}}{dz} \Big _{z=L_z} = 0$
$r_{shell}=0$	$\frac{\partial C_{i,shell}}{\partial r_{shell}} \Big _{r_{shell}=0} = 0$	-
$r_{shell}=d_{mt}/2$	$D_{r,i,shell} \frac{\partial C_{i,shell}}{\partial r_{shell}} \Big _{r_{shell}=\frac{d_{mt}}{2}} = k_{gs,shell} (C_{i,shell} - C_{p,i,shell}^{surf}) + k_{gs,shell} \frac{P_{i,surf}}{P} \frac{(C_{H_2,shell} - C_{H_2,\delta})}{1 - X_{H_2,\delta}}$ $D_{r,H_2,shell} \frac{\partial C_{H_2,shell}}{\partial r_{shell}} \Big _{r_{shell}=\frac{d_{mt}}{2}} = \frac{\varphi_0}{\delta_m} \exp\left(-\frac{E_{H_2}}{RT_{av}}\right) (P_{H_2,perm}^{0.5} - P_{H_2,shell}^{0.5})$	-

When the studies mentioned above are examined, the mass balance equations including the axial and radial dispersion are written for the transient conditions for the reaction (Eq. (2.101)) and permeation (Eq. (2.102)) sides.

- For Reaction Side:

$$\frac{\partial P_i^R}{\partial t} = D_{i,z} \frac{\partial^2 P_i^R}{\partial z^2} + D_{i,r} \frac{\partial^2 P_i^R}{\partial r^2} + RT_R \left(-\frac{\partial F_i^R}{\partial z} + \sum_{j=1}^{N_R} v_{i,j} r_j \right) \quad (2.101)$$

- For Permeation Side:

$$\frac{\partial P_i^P}{\partial t} = D_{i,z} \frac{\partial^2 P_i^P}{\partial z^2} + D_{i,r} \frac{\partial^2 P_i^P}{\partial r^2} - RT_P \frac{\partial F_i^P}{\partial z} \quad (2.102)$$

Table 2.21 shows the initial and boundary conditions used in two-dimensional mass balance equations for the reaction, permeation, tube, and annulus sides.

Table 2.21 The initial and boundary conditions for each side (Alavi et al., 2017)

Side	Condition	Equation
Reaction Side	Initial Condition	$P_i^R(z, r) \big _{t=0} = P_i^{R,initial}$
	Boundary Condition	$P_i^R \big _{z=0} = P_i^{feed}$
		$\frac{\partial P_i^R}{\partial z} \big _{z=L} = 0$
Permeation Side	Initial Condition	$P_i^P(z, r) \big _{t=0} = P_i^{P,initial}$
	Boundary Condition	$P_i^P \big _{z=0} = P_i^{sweep}$ (Co-current flow)
		$P_i^P \big _{z=L} = P_i^{sweep}$ (Counter flow)
		$\frac{\partial P_i^P}{\partial z} \big _{z=L} = 0$
Tube Side	Boundary Condition	$\frac{\partial P_i}{\partial z} \big _{r=r_{i,M}} = 0$ for $i \neq H_2$ $\frac{\partial P_i}{\partial z} \big _{r=0} = 0$
Annulus Side	Boundary Condition	$\frac{\partial P_i}{\partial z} \big _{r=r_{o,M}} = 0$ for $i \neq H_2$ $\frac{\partial P_i}{\partial z} \big _{r=r_{o,shell}} = 0$

➤ *Energy Balance*

In the modeling study of Kyriakides et al. (2013), the heat transfer between the reaction and permeation sides was neglected. Thus, the temperature in the permeation side was assumed as constant. In addition, it was assumed that there is no heat exchange between the reaction and permeation sides, the temperature of the wall was taken as constant. Thus, the energy balance equation in the reaction side is given as follows:

$$u\rho c_p \frac{\partial T}{\partial z} = k_r \left[\frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right] + \rho_b \sum_j r_j [-\Delta H_j] \quad (2.103)$$

where u , ρ , c_p , k_r , ρ_b , and ΔH are the velocity, the density of the gas mixture, the heat capacity of the gas mixture, the effective radial thermal conductivity (1.5 J/m·s·K), the density of catalytic bed, and the heat of reaction j , respectively. Table 2.22 shows the boundary conditions in the energy balance equations used in the study of Kyriakides et al. (2013).

Table 2.22 Boundary conditions used in the energy balance (Kyriakides et al., 2013)

Boundary	Reaction Side
$z = 0, \forall r$	$T = T_{in}$
$r = r_i, \forall z$	$k_r \frac{\partial T}{\partial r} = h_w(T_w - T)$
$r = r_o, \forall z$	$\frac{\partial T}{\partial r} = 0$

In another study, Cruz and Silva (2017) examined the energy balance equations for the reaction side (gas and solid phases) as two-dimensional and the permeation side as one dimensional. Firstly, for the reaction side, the energy balance equations of gas and solid phases are given in Eqs. (2.104) and (2.105), respectively.

$$\rho_{g,shell} C_{p_{g,shell}} \left(V_{g,r,shell} \frac{\partial T_{g,shell}}{\partial r_{shell}} + V_{sg,z,shell} \frac{\partial T_{g,shell}}{\partial z} \right) = 2\lambda_{g,r,shell} \frac{\partial^2 T_{g,shell}}{\partial r_{shell}^2} + \lambda_{g,z,shell} \frac{\partial^2 T_{g,shell}}{\partial z^2} - h_{gs,shell} \frac{(1-\varepsilon)}{\varepsilon} \frac{3}{R_p} (T_{g,shell} - T_{s,shell}) - h_w \frac{\pi d_{react}}{A_{react} \varepsilon} (T_m^{fg} - T_{g,shell}) ; 0 \leq z \leq L_z, 0 \leq r_{shell} \leq R_{shell} \quad (2.104)$$

$$\lambda_{s,r,shell} \frac{\partial^2 T_{s,shell}}{\partial r_{shell}^2} + \lambda_{s,z,shell} \frac{\partial^2 T_{s,shell}}{\partial z^2} = \rho_{cat,shell} \frac{(1-\varepsilon_p)}{\varepsilon_p} \sum_{j=1}^3 (-\Delta H_{fj,shell}) \eta_j R_j + h_{gs,shell} \frac{(1-\varepsilon)}{\varepsilon} \frac{3}{R_p} (T_{g,shell} - T_{s,shell}) ; 0 \leq z \leq L_z, 0 \leq r_{shell} \leq R_{shell} \quad (2.105)$$

where $\rho_{g,shell}$, and $\rho_{cat,shell}$ are the mixture and the catalyst densities on the shell side. $C_{p_{g,shell}}$ is the specific heat constant on the shell side. $T_{g,shell}$, $T_{s,shell}$, and T_m^{fg} are the gas temperature, the solid temperature, and the average wall temperature, respectively. $\lambda_{g,r,shell}$, $\lambda_{g,z,shell}$, $h_{gs,shell}$, and h_w are the gas thermal conductivity in the radial direction, the gas thermal conductivity in the axial direction, the gas-solid heat transfer coefficient, and the inside of the reactor wall heat transfer coefficient, respectively. d_{react} and A_{react} are the diameter and area of the reactor.

Secondly, the energy balance equation in the permeation side is given as follows:

$$\frac{dT_{perm}}{dz} = \frac{\pi d_{shell}}{Y_{H_2,perm} F_{CH_4,0} C_{p_{H_2}}^{perm}} \left[\frac{\varphi_0}{\delta_m} \exp\left(-\frac{E_{H_2}}{RT_{av}}\right) (P_{H_2,perm}^{0.5} - P_{H_2,shell}^{0.5}) C_{p_{H_2}}^{perm} + U \frac{d_{perm}}{d_{shell}} \right] (T_{g,shell} - T_{perm}) \quad (2.106)$$

where T_{perm} is the temperature on the permeation side. $C_{p_{H_2}}^{perm}$, U , d_{shell} , and d_{perm} are the heat capacity on the permeation side, the overall heat transfer coefficient, and the diameters on the shell and the permeation sides, respectively. Table 2.23 shows the inlet and boundary conditions for energy balance equations used in the study of Cruz and Silva (2017).

Table 2.23 The inlet and boundary conditions for energy balance equations (Cruz and Silva, 2017)

Boundary	Reaction Side	Permeation Side
z=0	$\lambda_{g,z,shell} \frac{\partial T_{g,shell}}{\partial z} \Big _{z=0} = \rho_{g,shell} C_{p,g,shell} (T_{g,shell} \Big _{z=0} - T_{op}^{in})$ (Gas Phase)	$T_{perm} \Big _{z=0} = T_{perm,0}$
	$\partial T_{s,shell} \Big _{z=0} = T_{op}^{in}$ (Solid Phase)	
z=L_z	$\frac{\partial T_{g,shell}}{\partial z} \Big _{z=L_z} = 0$ (Gas Phase)	$\frac{\partial T_{perm}}{\partial z} \Big _{z=L_z} = 0$
	$\frac{\partial T_{s,shell}}{\partial z} \Big _{z=L_z} = 0$ (Solid Phase)	
r_{shell}=0	$\frac{\partial T_{g,shell}}{\partial r_{shell}} \Big _{r_{shell}=0} = 0$ (Gas Phase)	-
	$\frac{\partial T_{s,shell}}{\partial r_{shell}} \Big _{r_{shell}=0} = 0$ (Solid Phase)	
r_{shell}=d_{mt}/2	$\lambda_{g,r,shell} \frac{\partial T_{g,shell}}{\partial r_{shell}} \Big _{r_{shell}=\frac{d_{mt}}{2}} = h_w (T_{g,shell} - T_m^{fg}) + J_{H_2} C_{p,H_2} (T_{g,shell} - T_m^{fg})$ (Gas Phase)	-
	$\lambda_{s,r,shell} \frac{\partial T_{s,shell}}{\partial r_{shell}} \Big _{r_{shell}=\frac{d_{mt}}{2}} = h_w (T_{s,shell} - T_m^{fg}) + J_{H_2} C_{p,H_2} (T_{s,shell} - T_m^{fg})$ (Solid Phase)	

When the literature studies mentioned above are examined, the energy balance equations for the tube (Eq. (2.107)) and annulus (Eq. (2.108)) sides are written according to the transient conditions as follows, and this term is zero when the steady-state condition is chosen.

- For Tube Side:

$$\sum_{i=1}^{N_s} C_i C_{p_i} \frac{\partial T_{tube}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C_{p_i} \frac{\partial T_{tube}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{tube}}{\partial z^2} \right] + \left[k_r \frac{\partial^2 T_{tube}}{\partial r^2} \right] + \psi \quad (2.107)$$

- For Annulus Side:

$$\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{an}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C p_i \frac{\partial T_{an}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{an}}{\partial z^2} \right] + \left[k_r \frac{\partial^2 T_{an}}{\partial r^2} \right] + \psi \quad (2.108)$$

In the Eqs. (2.107) and (2.108), the term, ψ , can be neglected according to the selection of the permeation side. Table 2.24 shows the initial and boundary conditions used in these energy balance equations for the tube and annulus sides.

Table 2.24 Initial and boundary conditions for the tube and annulus sides (Alavi et al., 2017)

Conditions	Reaction Side (Tube Side)	Permeation Side (Annulus Side)
Initial Conditions	$T_{tube} \big _{t=0} = T_{tube,initial}$	$T_{an} \big _{t=0} = T_{an,initial}$
Boundary Conditions	$T_{tube} \big _{z=0} = T_{feed}$	$T_{an} \big _{z=0} = T_{sweep}$ (Co-current flow)
		$T_{an} \big _{z=L} = T_{sweep}$ (Counter flow)
	$\frac{\partial T_{tube}}{\partial z} \big _{z=L} = 0$	$\frac{\partial T_{an}}{\partial z} \big _{z=L} = 0$ (Co-current flow)
		$\frac{\partial T_{an}}{\partial z} \big _{z=0} = 0$ (Counter flow)
	$q \big _{r=r_{i,M}} = -U_M(T_{tube} - T_{an}) + \phi$	$q \big _{r=r_{i,shell}} = -U_{shell}(T_{an} - T_{oven})$
	$\frac{\partial T_{tube}}{\partial r} \big _{r=0} = 0$	$q \big _{r=r_{o,M}} = -U_M(T_{tube} - T_{an}) + \phi$

➤ Momentum Balance

The momentum balance equations are required to calculate the pressure drop in both sides of the MR. In 2-D models, generally, the non-isobaric condition is assumed for the reaction side, while the isobaric condition is assumed for the permeation side. When the 2-D modeling studies in the literature are investigated, in general, the momentum equations are solved as 1-D for the reaction side. For example, Kyriakides et al. (2013) assumed that the pressure in the permeation side was constant. The change of pressure in the reaction side was investigated as one-dimensionally. In another modeling study, De Falco et al. (2008) solved the momentum balance equation in the reaction side as one-dimensionally, and the pressure drop in the permeation side was neglected. In these studies, the momentum balance equations in the reaction side were calculated using Ergun equations given in Momentum Balance part of Section 2.7.1.1.

In some 2-D modeling studies such as Gallucci et al. (2010) and Said et al. (2015), the momentum balance equations are solved according to both axial and radial

directions. For example, Gallucci et al. (2010) solved the momentum equation with the dynamic condition, whereas Said et al. (2015) solved the same equation with the steady-state condition. The momentum balance equation used in both studies is given as follows:

$$\frac{\partial}{\partial t}(\varepsilon \rho \bar{u}) + \nabla \cdot (\varepsilon \rho \bar{u} \bar{u}) = -\varepsilon \nabla p - \beta \varepsilon \rho \bar{u} - \nabla \cdot (\varepsilon \bar{\tau}) + \varepsilon \rho g \quad (2.109)$$

where ε is the porosity and assumed as constant in Said et al. (2015). ρ is the density and $\bar{\tau}$ is the stress tensor. β and $\bar{u}$ are the mixture velocity and the friction coefficient, and they are calculated using Eqs. (2.110) and (2.111), respectively.

$$\beta = 150 \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{\mu}{\rho d^2} + 1.75 \frac{1-\varepsilon}{\varepsilon^3} \frac{\varepsilon \bar{u}}{d} \quad (2.110)$$

$$\bar{u} = \sqrt{u_r^2 + u_z^2} \quad (2.111)$$

➤ Comparison of 2-D Membrane Reactor Models

Table 2.25 shows the summary of 2-D MR modeling studies for hydrogen production from methane in the literature. Except for the study of Gallucci et al. (2010), all studies were solved for the steady-state condition. Generally, for the reaction side, the mass and energy balance equations were examined as two-dimensionally, and the momentum balance equations were examined as one-dimensionally. However, the mass and energy balance equations in the permeation side were written with the assumption that they only change through the axial direction. In all the studies given in Table 2.25, the momentum balance equations in the permeation side were not considered, since the pressure was assumed as constant through the reactor.

Table 2.25 The summary of 2-D membrane reactor modeling studies found in the literature

Ref.	Flow Type	Reaction Side	Balance Equations						Validation
			Mass		Energy		Momentum		
			R	P	R	P	R	P	
(Kyriakides et al., 2016)	Counter-current	Shell							Experimental
(Ghouse and Adams, 2013)	Co-current	Tube							Theoretical
(Cruz and Silva, 2017)	Co-current	Shell							None
(Kyriakides et al., 2013)	Co-current	Shell							Theoretical
(De Falco et al., 2008)	Counter-current	Shell							None
(Gallucci et al. 2010)	Co-current	Tube							None
(Said et al., 2015)	Counter-current	Shell							Experimental
(Rodríguez et al., 2012)	Co-current	Tube							Theoretical
(Saidi, 2018)	Co-current	Tube							Experimental and Theoretical

In recent years, a few studies related to the 2-D modeling of membrane reactors that produces hydrogen through steam methane reforming are found in the literature. For example, Kuncharam et al. (2020) developed a multi-scale 2-D model of a packed bed membrane reactor that produces hydrogen from steam methane reforming. This model includes mass and energy equations for the fluid-phase in the axial and radial dispersions, as well as the resistances of mass and heat at the boundary of the fluid-solid phase. In this model, three pressure drop equations (Ergun equation that neglects the effects of the wall, Einfeld-Schnitzlein, and Di Felice-Gibilario correlations) were used and their effects on the performance were compared. The results showed that when the Ergun equation is used, the pressure drop and the linear velocity are found to be higher than the others, however, this equation has no effect on the other variables. Therefore, the Ergun equation gives satisfactory results for the steam methane reactions and their conditions, and it was found that taking account of wall effects does not provide any gains. Murmura et al. (2021) studied the derivation of enhanced Sherwood number taking into account the changes of each species through reactor length in the reaction and permeation sides. The Sherwood number expression was defined from the radial gradients of hydrogen concentration derived from the combination of reaction and permeation through the membrane. Therefore, the

simplified 2-D model of membrane reactor was developed using the COMSOL Multiphysics program. The results showed that the developed model is enough for describing of the system compared to more complete 2-D models.

2.7.2.3 Three-Dimensional Model

In a 3-D MR model, the balance equations given in Table 2.13 are regulated according to the cylindrical coordinate system and these equations are generally solved using software such as AnsysTM Fluent, COMSOL Multiphysics, and MATLAB. Figure 2.18 shows the geometry of a tubular MR used in the three-dimensional modeling approach.

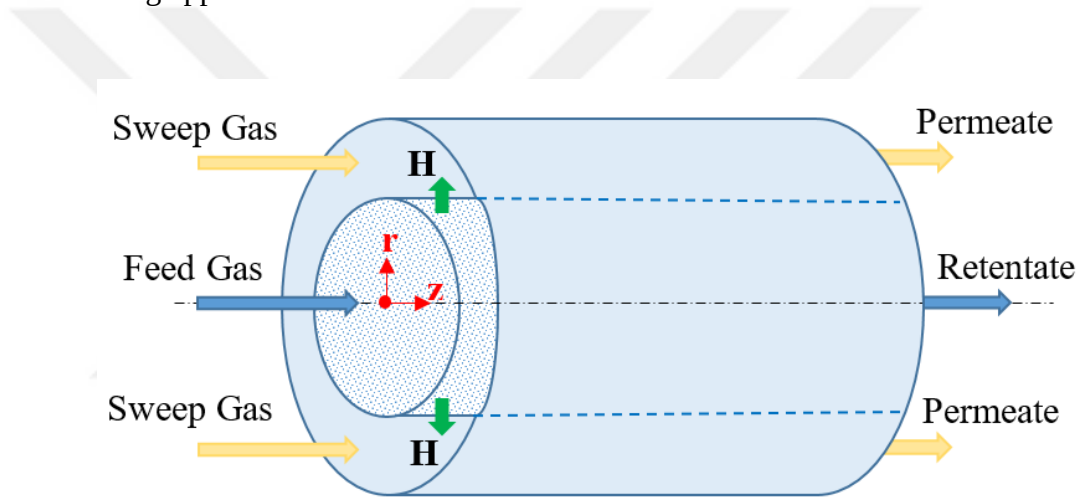


Figure 2.18 The geometry of a tubular MR used in the three-dimensional modeling approach

According to the authors' knowledge, no studies on the 3-D modeling of a MR for hydrogen production from methane exist in the literature. However, in the literature, some studies on the 3-D modeling of MRs that produce hydrogen from different chemical reactions, such as methanol steam reforming (Ribeirinha et al., 2017), water gas shift (Muruganandam, 2011; Chein et al., 2014), ethanol steam reforming (Yang et al., 2020), are found.

2.7.2.4 Comparison of Different Dimensional Models

As mentioned in Sections 2.7.1.1, 2.7.1.2, and 2.7.1.3, in the literature, 1-D, 2-D, and 3-D MR modeling studies are found in different complexity. Although 1-D models

have mass and heat transfer limitations in the radial direction, these models provide enough information to understand the operation of industrial applications (Ma et al., 2016). However, 2-D models provide more realistic results compared to 1-D models. However, 3-D models yield the closest results to the exact results among these modeling approaches. In the literature, some comparison studies for 1-D, 2-D, and 3-D MR models can be found. For example, Oyama and Hacıoğlu (2009) studied the development of both 1-D and 2-D models. Their results showed that the two-dimensional model gives a better match with the experimental results compared to the 1-D model. Marin et al. (2012) developed a 2-D MR model including mass, energy, and momentum balance equations. This model was validated with experimental data, and it was found that this 2-D model could predict the methane conversion with a 10% deviation from the experimental data. Then, a simplified one-dimensional model was investigated in comparison to the 2-D model to assess whether 1-D gives accurate enough results. The results of their study showed that the 2-D model should be preferred to simulate heat transfer in both radial mass and radial in more detail. Pashchenko (2018) conducted a comparison study for 1-D, 2-D, and 3-D models of a MR using ANSYS Fluent software. It was found that, when 2-D and 3-D models are used, the difference in the results is not significant compared to the difference in the results when 1-D and 3-D models are used. They concluded that if the residence time and the relative length have a value higher than 8 kg_{cats}/mol and 15, respectively, a one-dimensional model can be sufficient for the calculations, otherwise, 2-D and 3-D models should be used.

2.8 Membrane Reactor Systems

MRs provide better performance in terms of higher conversion and hydrogen yield with respect to CRs, in the meantime recovering a high or low grade hydrogen stream (permeate side) depending on the hydrogen perm-selectivity characteristics of the used membrane, and then the hydrogen stream can be used later in the fuel cell applications. Moreover, the non-permeated or retentate stream with high CO₂ content is used in the CO₂ capture systems and then the captured CO₂ can be used in the different systems (e.g., power-to-gas technologies or fuel production) (Lu and Xie, 2016; Iulianelli et

al., 2016c, Nalbant Atak et al., 2021). The integration of MRs into the hydrogen production plants provides the promising advantages related to the environmental and improving energy goals. The integration system technically reduces the coal requirements and thus the CO₂ emission levels by the intensification of process and the high efficiency of carbon capture. Moreover, the integration of MRs and CO₂ capture system provides the elimination of over plus components such as the conventional water-gas shift reactors, and separation units. Consequently, the integrated system including a MR also increases the economic performance of the system (Ma et al., 2015). For example the MRs provide to improve hydrogen production processes and increase hydrogen efficiency with the unique ability of the MRs that carry out simultaneously the hydrogen generation and purification in a single-stage process. In contrast, at the same time, the hydrogen production by steam methane reforming process can cause CO₂ emissions due to the amount of CO₂ in the retentate stream, and this can be also a concern in the world. However, MRs provide that the concentrating CO₂ in the retentate stream is to be further captured in the second stage processes. Therefore, the MRs integrated with the CO₂ capture systems can lead to making CO₂ useful in the future.

In the literature, some studies related to integration of MRs with different systems (fuel cells applications and CO₂ capture systems) can be found. According to the literature survey for the fuel cell systems, for example, Ribeirinha et al. (2018) conducted the experimental and modeling studies related to HT-PEMFC integrated with cellular membrane providing methanol steam reforming. 3-D non-isothermal model of this sytem were developed using Fluent (AnsysTM) software. In this study, firstly this model was validated with the experimental data, then the effects of some parameters (temperature and pressure) were investigated. In addition, the results of the polarization curves for HT-PEMFC fed with pure hydrogen and PBMR/HT-PEMFC system were compared and it is found that the performances are same and Pd-Ag membrane is fully hydrogen selective membrane. Loreti et al. (2019) created four difference case studies according to the placements of selective membrane. Case 1 is steam reforming and water-gas shift reactors with PSA purification unit, Case 2 is steam reforming and water-gas shift reactors with selective membrane, Case 3 is steam

reforming reactor and membrane integrated water-gas shift reactor, and Case 4 is membrane integrated steam reformer reactor. In this study, the effects of the placements of membrane on the fuel processing efficiency, global efficiency, and thermal efficiency were investigated, and compared. The best efficiency values were found for Case 4, and the fuel processing efficiency, global efficiency, and thermal efficiency were calculated as 83.8%, 38.4%, and 61.5%, respectively. Di Marcoberardino et al. (2018) studied the economical and environmental analysis of a micro-CHP system that consists of an auto-thermal membrane reactor and PEM fuel cell. These analysis were done according to six different scenarios including three different residual loads in 2 countries (Germany and Italy) in order to examine the effects of thermal and electrical loads and natural gas and electricity costs on the results. Then, the results for ATR-MR and conventional SR were compared. The efficiency of ATR-MR was found as 42%, while the efficiency of conventional SR was found as 33%. Thus, in this case, it can be said that ATR-MR has lower environmental effects than the conventional SR. However, the evaluate of only environmental effects may not give correct results. When the cost analysis was investigated, it is found that the costs for ATR-MR can change from 240 €/kW to 17,620 €/kW depending on application and location, whereas the cost of conventional SR system was lower. Parvasi et al. (2020) developed 1-D model of membrane reactor system that provides hydrogen production and separation for fuel cell vehicles. The performance and flexibility of fuel processor were examined according to the different water-methane ratio and reaction pressure. The results demonstrated that this system produces 5 kg/day of pure hydrogen for 500 km range. To produce 1kg of pure hydrogen, the total requirement amounts of methane and water were calculated as 50 kg and 70 kg, respectively.

According to the literature survey for the CO₂ capture systems, for example, Ma et al. (2015) studied an assessment of the economic performance for the integrated systems including a MR with and without CO₂ capture system. In this study, the comprehensive net present value model was developed using a Monte Carlo simulator to evaluate the economic performance. The results showed that when the price of carbon rises in the future, ranking from largest to smallest for the degree of sensitivity

of economic performance was found as: hydrogen production using PSA without carbon-capture system > hydrogen production using PSA with carbon-capture system > hydrogen production using a membrane reactor. The lower the sensitivity, the better the economic performance. Kim et al. (2018) examined an experimental study related to hydrogen production from a MR with Pd-based composite membrane. The aim of this study is to investigate the composition of the outlet gases from the membrane reactor and to determine whether it is appropriate for CO₂ capture. The results showed that the gas composition in the permeation side was consisted of 97.8 vol% of hydrogen, whereas the gas compositions in the reaction side was consisted of 67.8 vol% of carbon dioxide with 22.2 vol% of methane. It can be deduced that when the MR is integrated into the CO₂ capture system, the energy can be recovered by the combustion of methane in the reaction side, and then CO₂ capture can be accomplished. Shirasaki and Yasuda (2013) investigated a case study related to hydrogen production and CO₂ capture in Tokyo Gas Company. This company developed a large-scale MR system that has 40 Nm³/h nominal hydrogen production capacity. The off-gas including high CO₂ concentration (90%) can easily be liquefied and captured. Therefore, this company designed and assembled CO₂ capture apparatus that includes a gas compressor, gas-liquid separator, chiller, and tank. This system was integrated with the large-scale MR system. The results showed that total CO₂ emissions for hydrogen production were reduced by 50% with only 3% energy loss. The overall system efficiency was found as 81.4% for hydrogen production without CO₂ capture system. When the low temperature CO₂ capture system was added, the efficiency decreased to 78.6%.

CHAPTER THREE

EXPERIMENTAL STUDY

3.1 Introduction

This chapter presents the conducted experimental studies carried out within the scope of the thesis. The Institute of Membrane Technologies (CNR-ITM) in Italy was visited for a period of 1 month between 11/10/2021-9/11/2021. During the experimental studies, the leakage tests, calibration tests, and permeation tests were done and investigated for different gases through the Pd/Al₂O₃ membrane, whereas the reaction tests were not conducted due to the technical problems in CNR-ITM.

3.2 Experimental Studies Conducted

During the experimental studies, reaction tests could not be performed due to the technical problems at the Institute, and experimental studies were carried out by performing the calibration and permeability tests of the Pd/Al₂O₃ membrane (Figure 3.1-(a)) only for the stainless-steel membrane separator module (Figure 3.1-(b)).

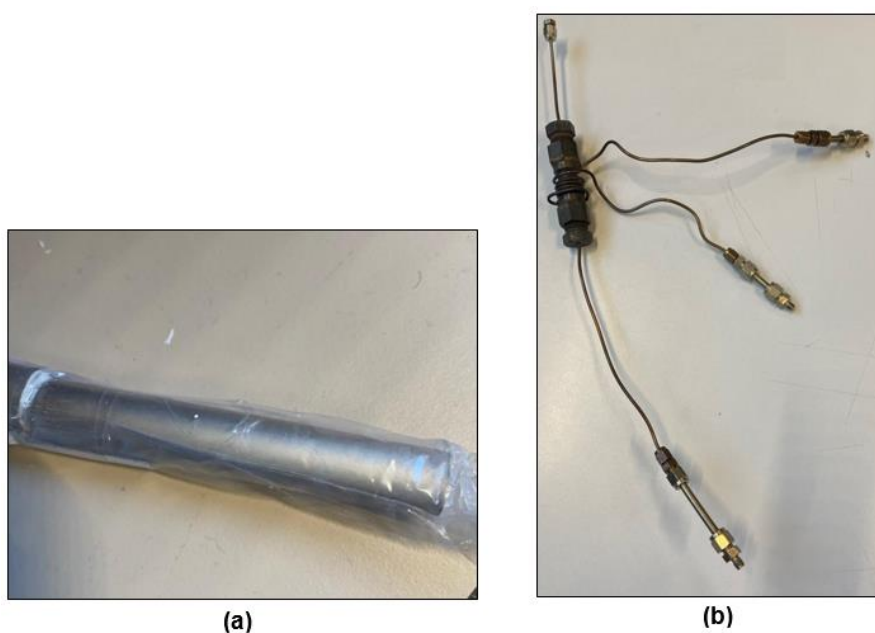


Figure 3.1 (a) Pd/Al₂O₃ membrane and (b) membrane separator module used in experimental studies

The module given in Figure 3.1-(b) is also used as a module for membrane reactors. Membrane separator has no catalyst side, thus the chemical reactions cannot take place and hydrogen cannot be produced, whereas membrane reactors provide both hydrogen production and hydrogen separation. During the experimental studies, since reaction tests cannot be examined for technical reasons, the purpose of these experimental studies was to investigate the membrane performance by performing calibration and permeability tests before reaction tests.

This module has 4 gas ports that are 2 inputs and 2 outputs. The purpose of experimental is to examine the passage of different gases through the Pd/Al₂O₃ membrane by performing permeability tests at different temperatures and pressures. An inlet connection is kept closed automatically, as there is no need to use sweep gas in the membrane separator module. Sweep gas is an inert gas that increases the "driving force", which helps the hydrogen produced in the reaction side in membrane reactors to be separated quickly after it passes into the permeation side. Other connection points are determined as feed gas inlet, permeate gas outlet and retentate gas outlet.

Before starting the permeation tests, firstly a leakage test must be performed to observe whether any gas leakage for the membrane separator module. If there is no leakage, then calibration tests can be performed for each gas. Gases used in experimental studies are methane (CH₄), carbon dioxide (CO₂), nitrogen (N₂) and hydrogen (H₂).

3.2.1 Leakage Test

The purpose of the leakage test is to prevent gas leaks that decrease the performance of the membrane during calibration and permeability tests. Therefore, before any test in membrane reactors or separators, a leakage check should be done as the first step. Schematic of a membrane separator for leakage testing is given in Figure 3.2.

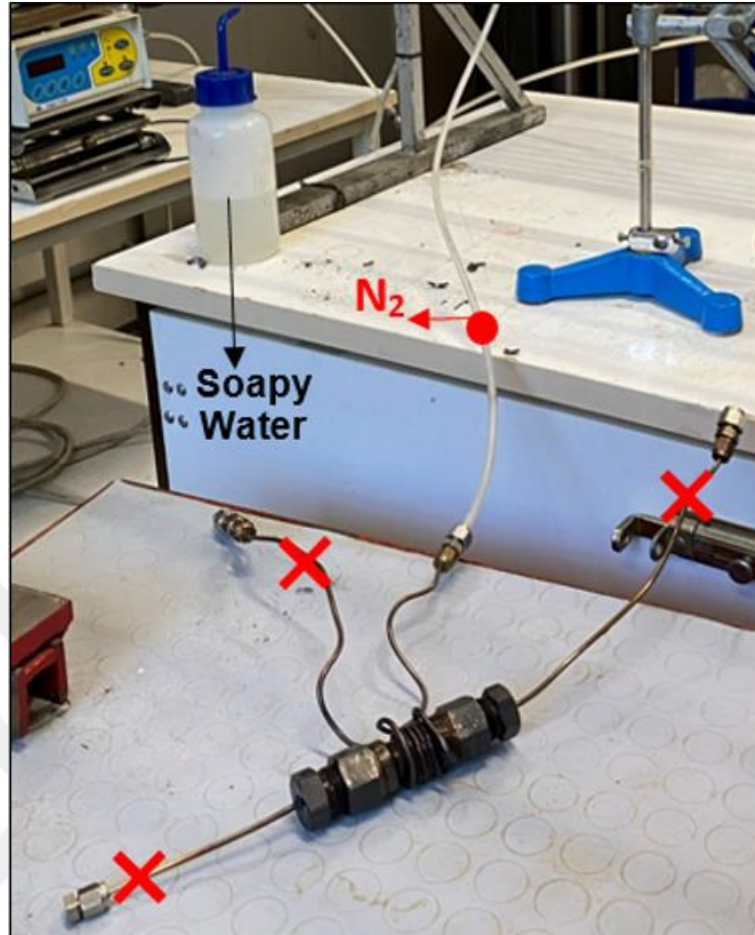


Figure 3.2 Schematic of a membrane separator for leakage testing

When Figure 3.2 is examined, N_2 was sent to the membrane separator from feed gas inlet connection point, and the other 3 gas connections were closed. Then, soapy water was sprayed on all connection points in the membrane separator assembly, and it was observed whether bubbles were formed at these points. The formation of bubbles means that the gas leaking with the passage of nitrogen occurs bubbles with the soapy water. It is important for accurate tests and measurements. If the leakage is observing, the connection points are strengthened by applying torque again to the sealing areas.

3.2.2 Integration of the Membrane Separator Module to the System

After the leakage test, gas connections were made from the connection points of system to the inlet and outlet points of the membrane separator for the calibration test. Figure 3.3 shows the schematic of the system used in the calibration test. As can be

seen in Figure 3.3, four different gases are sent to the system from four different mass flow controllers and the feed gas is formed by mixing these gases. The feed gas is fed to the membrane separator and the permeate gases through the membrane come to the bubble flow meter, and then the volumetric flow rates are calculated using bubble flow meter, whereas the retentate gases through the membrane are released back to the atmosphere. The yellow arrows in Figure 3.3 indicate that gases were released into the atmosphere. The feed gas valve is set to be sent both to the system and to the atmosphere, this is used to prevent high pressure increases. The controller that adjusts the valve opening sets the valve of the mass flow controller from 1% to 100% for each gas. Calibration and permeation tests are made according to the adjusted valve opening percentages.

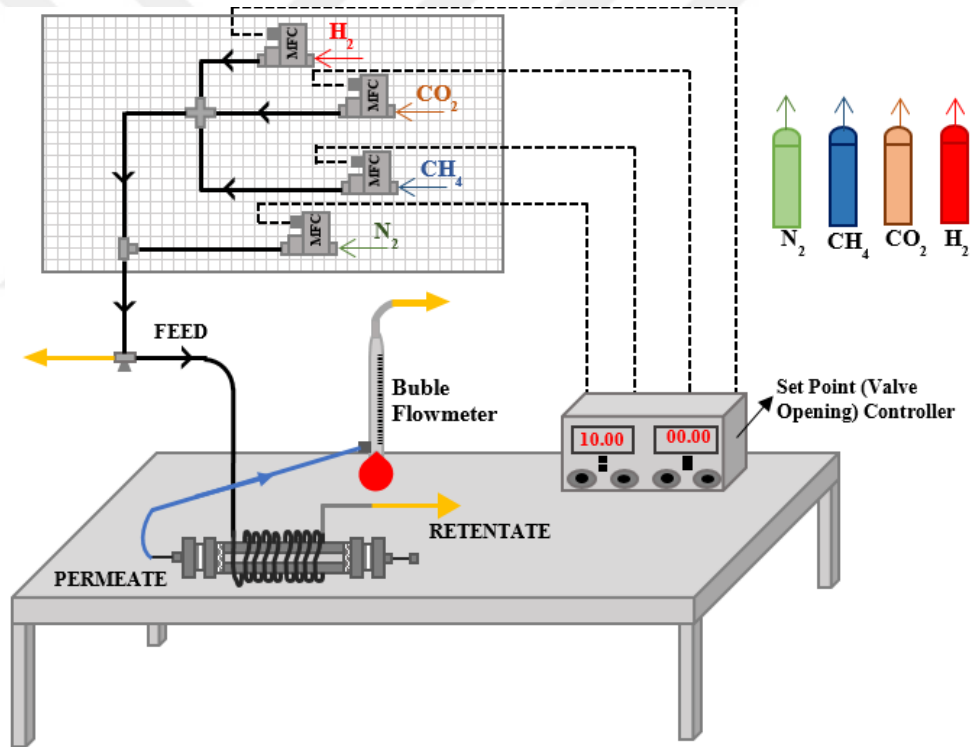
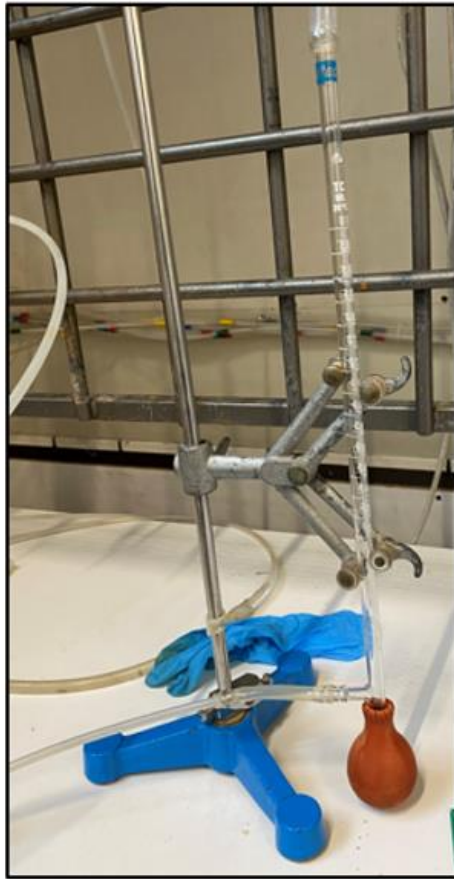


Figure 3.3 Schematic of the system used in the calibration test

3.2.3 Calibration Tests

Firstly, a leak test should be applied to the system in order to calibrate the components and fasteners used in the system. Before proceeding with the permeability tests, the calibration test is an important step to understand whether properly operations

of the mass flow controllers according to the valve opening. Calibration is defined as the measurement comparison between the measurements from device and the reference device. While performing the calibration test, each gas is sent to the system separately. For example, while nitrogen is sent to the membrane separator module, the mass flow controllers of other gases should be closed and there is no gas flow from there. Then, only nitrogen comes as the feed gas and enters the separator from the feed gas inlet, and the permeated nitrogen through the membrane comes to the bubble flow meter and the volumetric flow rates are calculated according to the different valve openings (1-100%). Figure 3.4 shows the devices used to calculate volumetric flow rates.



(a)



(b)



(c)

Figure 3.4 Devices used in the calculation of volumetric flow rates; (a) bubble flow meter, (b) valve opening controller, and (c) chronometer

To calculate volumetric flow rates, a bubble flow meter, valve opening controller and chronometer are used. The gas to be used for calibration is sent as the feed gas alone, and the valve opening controller was changed from 1% to 15% (one each), 15% to 50% (five each), and finally 50% to 75% (twenty-five each). Calculation is made for each value by increasing. For a volume selected depending on the gas passage rate, the time for the gas to pass through the determined volume was measured 5 times and the average of these times was calculated. Thus, volumetric flow rates are calculated using Eq. (3.1).

$$Q(\text{mL}/\text{min}) = \frac{\text{Volume (mL)}}{\text{time (s)}} \times 60 \frac{\text{s}}{\text{min}} \quad (3.1)$$

If an example calculation is made for nitrogen, while the valve opening was 4%, the time was measured 5 times from the chronometer for the 1 mL volume, and the measured times were found 13.3 s, 13.6 s, 13.5 s, 13.6 s and 13.3 respectively. The mean time was calculated as 13.51 s. Consequently, when these values are substituted in Eq. (105), the volumetric flow rate was calculated as 4.44 mL/min while the valve opening was 4%. All calculations were made according to each valve opening for each gas. Figure 3.5 shows the change of volumetric flow rates depending on the valve opening for each gas according to the calibration test results.

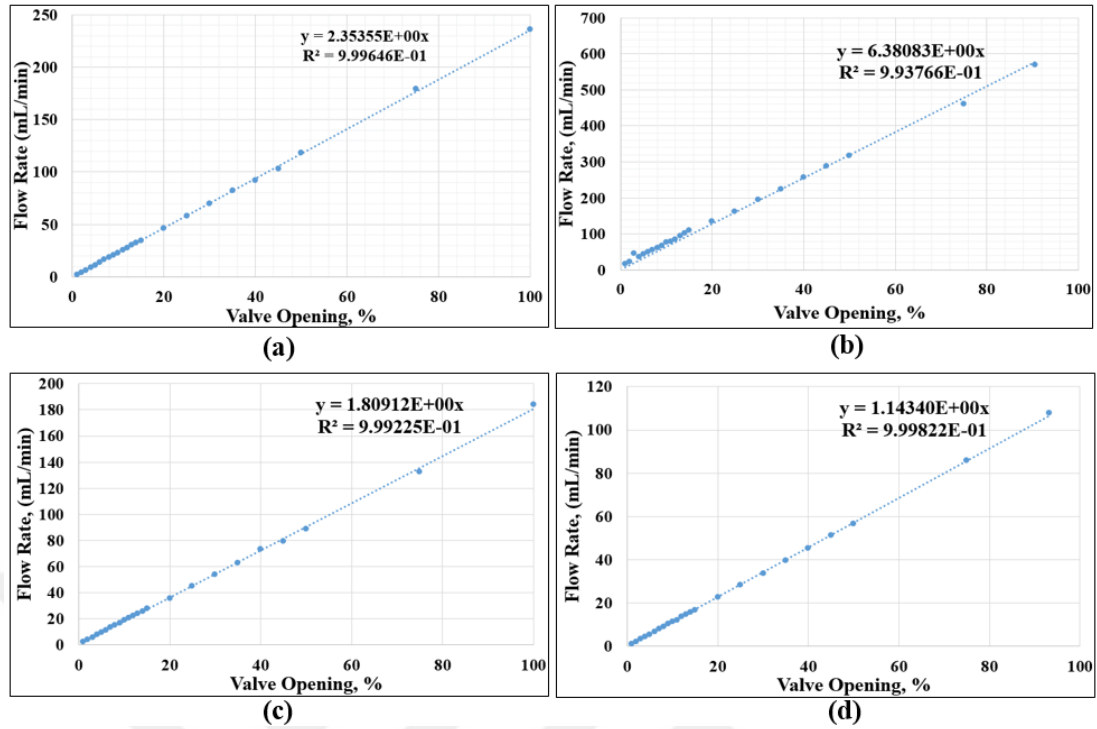


Figure 3.5 Change of volumetric flow rates according to valve opening percentages for each gas; (a) H₂ gas, (b) CO₂ gas, (c) CH₄ gas, and (d) N₂ gas

As can be seen in Figure 3.5, the regression coefficients were determined according to the graph of the calculated volumetric flow rates depending on the valve opening percentages. The regression coefficient is a statistical coefficient used to estimate the relationship between the dependent variable and the independent variable. The closer this coefficient is to 100%, the better the fit between the two variables. These values were found to be 0.997, 0.937, 0.992 and 0.998 for hydrogen, carbon dioxide, methane and nitrogen, respectively. When the results for each gas were examined, it was observed that the mass flow controllers and valve opening controllers were operating properly.

3.2.4 Permeation Tests

Single gas permeability tests were performed at CNR-ITM using a custom-made stainless steel membrane separator placed in bench scale experimental setup. The membrane module has a length of 12 cm and an outer diameter of 3 cm. The length of the Pd/Al₂O₃ membrane is 8 cm and the outer diameter is 13 mm. The membrane was

placed inside the module and two graphite gaskets were added and blocked at both membrane ends to prevent mixing of permeate and retentate streams. While conducting the permeability tests, the membrane separator module was placed in the furnace and kept at a constant temperature of 400°C, and the absolute feed pressure was carried out using single gases such as H₂, N₂, CO₂ and CH₄, varying between 0.5 bar and 3 bar. In this experimental study, permeation tests could only be performed for 400°C due to the limited time.

The mentioned above gases were sent from the thin cylinders to the membrane separator module by controlling the volumetric flow rates using mass flow controllers. The membrane separator module was heated by placing it in a furnace and N₂ was introduced as an inert gas at ambient pressure until set temperature conditions (400°C) were achieved as measured by a K-type thermocouple. The inlet pressure was kept constant at 1 bar, while the feed gas pressure was controlled by a back pressure controller located at the outlet of the retentate. For this temperature, the volumetric flow rate through the membrane was measured with a bubble flowmeter relative to the varying pressure and percentages of valve opening. In Figure 3.6, the experimental setup used for the permeation tests is shown.



Figure 3.6 Experimental setup

While performing the permeation tests, the pressure difference between the feed gas (P_{feed}) and the permeate gas ($P_{permeate}$) is adjusted with the pressure gauge located at the retentate outlet. In the experiments, the permeation gas pressure was taken as constant and 1 bar. The feed gas pressure is calculated using Eq. (3.2).

$$P_{feed} = P_{set\ pressure} + P_{permeate} \quad (3.2)$$

The following equation is used to calculate the permeation flux through membrane (J_i) for each gas during the permeation tests.

$$J_i \left(\frac{\text{mol}}{\text{min} \times \text{m}^2} \right) = \frac{Q_i}{A_{\text{membrane}}} \left(\frac{\text{mL}}{\text{min} \times \text{m}^2} \right) \times \frac{10^{-3} \text{L}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{22.414 \text{ L}} \quad (3.3)$$

where Q_i is defined as the volumetric flow rate for each i gas ($i = \text{N}_2, \text{H}_2, \text{CO}_2$ and CH_4) calculated by the bubble flowmeter. A_{membrane} is defined as the surface area of the membrane and is calculated by the equation. $2\pi r_{\text{mem}} L_{\text{mem}}$. The following unit conversion equations are used to unit convert from volumetric flow rate to molar flux.

$$1 \text{ mol gas} = 22.414 \text{ L} \quad (3.4)$$

$$1 \text{ L} = 1000 \text{ mL} \quad (3.5)$$

When the furnace was fixed at 400°C, it was waited overnight by simply passing nitrogen through the system. The next day, permeation tests were started. Approximate measurements were made using a bubble flow meter and a chronometer according to the pressures selected within 4 to 5 hours. At each gas exchange, it must be fed with new gas for approximately 1 hour in order to completely separate the other gas from the membrane separator module. The selected gas and its date during the permeation tests are given in Table 3.1.

Table 3.1 The gases used in the permeation test and the dates of the measurement

Gas	Date
Nitrogen (N ₂)	29/10/2021
Hydrogen (H ₂)	02/11/2021
Carbon dioxide (CO ₂)	02/11/2021
Methane (CH ₄)	03/11/2021
Hydrogen (H ₂)	03/11/2021

In Figure 3.7, the graph of permeating flux through the membrane is given for each gas measured during the permeation tests, depending on the changing pressure. The measurements and wait at least 1 hour between the two gases. In the permeation tests, the first measurements were made for nitrogen and the results are given in Figure 3.7-(a). Then, on 02/11/2021, only hydrogen was fed for 1 hour before starting the measurements for hydrogen, and measurements were made after the remaining nitrogen in the module was removed, and the results are given in Figure 3.7-(b).

Similar measurements were made in carbon dioxide and methane at different pressures, and the results are given in Figure 3.7-(c) and Figure 3.7-(d), respectively.

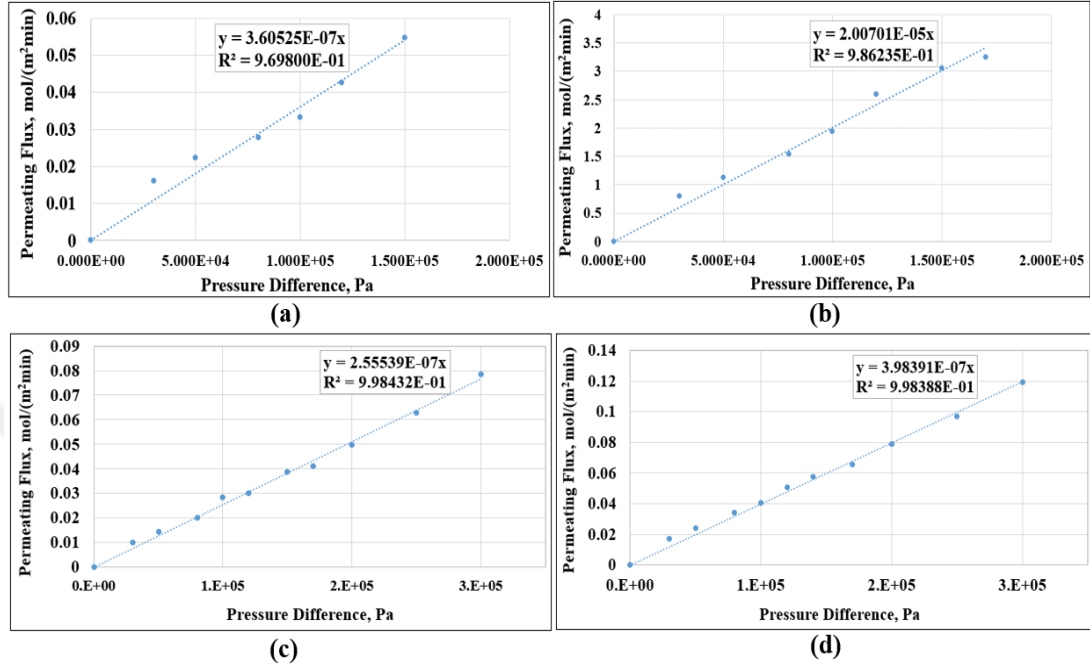


Figure 3.7 The change of the permeating flux through membrane according to different pressure differences in the permeation tests; (a) N₂ - 29/10/2021, (b) H₂ - 02/11/2021, (c) CO₂ - 02/11/2021 and (d) CH₄ - 03/11/2021

After all measurements were completed, in order to recalculate the permeation flux of hydrogen through the membrane, a permeation test was again performed after approximately 2 hours of hydrogen feeding, and the results are given in Figure 3.8. Using these last results, the ideal selectivity of hydrogen in other gases was calculated according to different pressure values and the results are given in Table 3.2. The ideal selectivity of hydrogen in other gases ($\alpha_{H_2,i}$) is calculated using the following equation.

$$\alpha_{H_2,i} = \frac{J_{H_2}}{J_i} \quad (3.6)$$

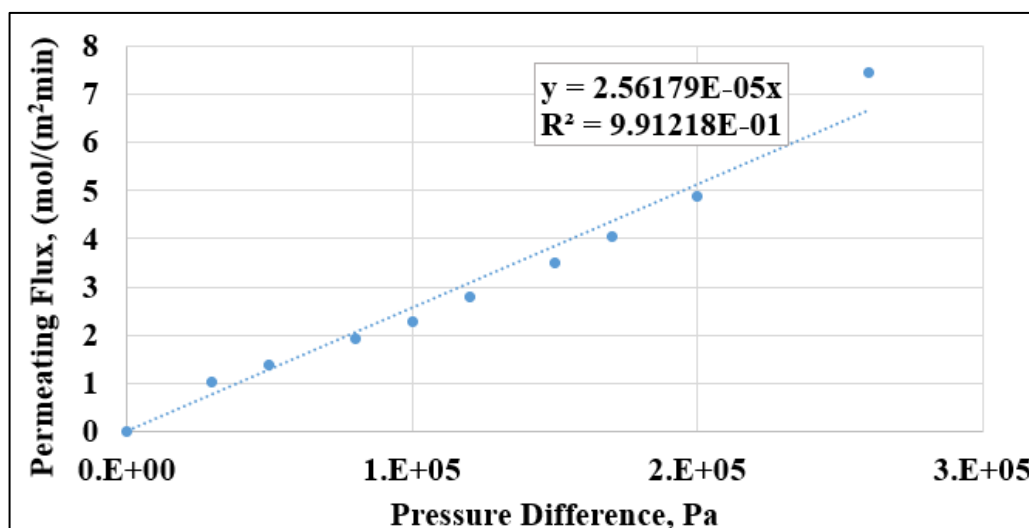


Figure 3.8 The change of permeating hydrogen flux through the membrane according to the changing pressure difference

Table 3.2 Ideal selectivities of hydrogen over other gases according to the changing pressure difference

Pressure		Ideal Selectivity			
DP, bar	DP, Pa	H ₂ /CH ₄	H ₂ /CO ₂	H ₂ /N ₂ for N ₂ 29-10-2021	H ₂ /N ₂ for N ₂ 27-10-2021
0.3	30000	60.28	101.48	63.80	-
0.5	50000	58.02	95.76	61.81	51.57
0.8	80000	56.03	95.49	69.26	-
1	100000	55.75	79.81	68.23	59.74
1.2	120000	55.44	93.40	65.93	-
1.5	150000	-	90.99	64.39	67.01
1.7	170000	61.94	98.53	-	-
2	200000	62.19	98.12	-	62.66

In Table 3.2, when the ideal selectivity values for nitrogen calculated according to the measurement results on two different dates are examined, it is observed that the next measurement is higher. Since the membrane used in the experiments is a supported membrane (composite membrane), not only hydrogen but also other gases pass through the membrane. For this reason, the ideal selectivity of hydrogen was calculated to be lower than that of self-supported membranes.

The perm-selectivity of hydrogen is limited when supported Pd-based membranes are used. In this case, not only hydrogen, but also other gases can pass through the membrane in small quantities. Therefore, using the hydrogen flux changing values

given in Figure 3.8, the total hydrogen flux through the membrane ($J_{H_2, total}$) is calculated with the following equation (Amiri et al., 2020).

$$J_{H_2, total} = \frac{1}{\frac{1}{J_{H_2}^{SD}} + \frac{1}{J_{H_2}^K} + \frac{1}{J_{H_2}^{HP}}} \quad (3.7)$$

where $J_{H_2}^{SD}$ represents the hydrogen flux through the membrane due to the solution/diffusion mechanism. $J_{H_2}^K$ represents the hydrogen flux through the membrane due to the Knudsen diffusion mechanism. $J_{H_2}^{HP}$ represents the hydrogen flux through the membrane due to the Hagen-Poiseuille mechanism. The hydrogen flux $J_{H_2}^{SD}$ through the Pd membrane due to the solution/diffusion mechanism is calculated by the following equation (Amiri et al., 2020):

$$J_{H_2} = \frac{B_{H_2}}{\delta} (P_{H_2, retentate}^n - P_{H_2, permeate}^n) \quad (3.8)$$

where B_{H_2} represents the hydrogen permeability, δ the membrane thickness, $P_{H_2, retentate}$ and $P_{H_2, permeate}$ represent the hydrogen partial pressures in the reaction and permeation sides. “n” is defined as the pressure exponent and varies between 0.5 and 1. B_{H_2} is calculated with the Arrhenius function as follows:

$$B_{H_2} = B_{H_2}^0 \cdot \exp\left(\frac{-E_m}{R \cdot T}\right) \quad (3.9)$$

where $B_{H_2}^0$ represents the pre-exponential factor, E_m the activation energy for the permeability, T the temperature, and R the universal gas constant. If the hydrogen bulk diffusion is the rate-limiting step that controls the permeation process, the value of n in Eq. (3.8) becomes 0.5 and the equation is rewritten as follows according to the Sieverts-Fick law (Amiri et al., 2020).

$$J_{H_2} = \frac{B_{H_2}}{\delta} (P_{H_2, retentate}^{0.5} - P_{H_2, permeate}^{0.5}) \quad (3.10)$$

The hydrogen flux through the membrane due to the Knudsen diffusion mechanism ($J_{H_2}^K$) and the hydrogen flux through the membrane due to the Hagen-Poiseuille mechanism ($J_{H_2}^{HP}$) are calculated using the following equations (Amiri et al., 2020).

$$J_{H_2}^K = \frac{\varepsilon d_p}{\tau L} \left(\frac{8}{9\pi MRT} \right)^{1/2} \Delta p_{H_2} \quad (3.11)$$

$$J_{H_2}^{HP} = \frac{r^2}{8\eta L P_0} P_{ave} \Delta p_{H_2} \quad (3.12)$$

where ε is the membrane porosity, d_p is the pore diameter, τ is the tortuosity, L is the thickness, M is the molecular weight of the diffusion gas, Δp_{H_2} is the transmembrane hydrogen partial pressure, η is the viscosity, P_{ave} average pressure, P_0 outlet pressure, and r is the radius. Since the membrane used in the experiment is the Pd/Al₂O₃ membrane (supported membrane), we require to find the most appropriate “n” value in order to calculate the total hydrogen flux permeating through the membrane. Therefore, by changing the n value between 0.5 and 1, using the hydrogen flux values given in Figure 3.8, the graphs drawn according to the change in transmembrane pressure difference ($P_{H_2,retentate}^n - P_{H_2,permeate}^n$) are given in Figure 3.9.

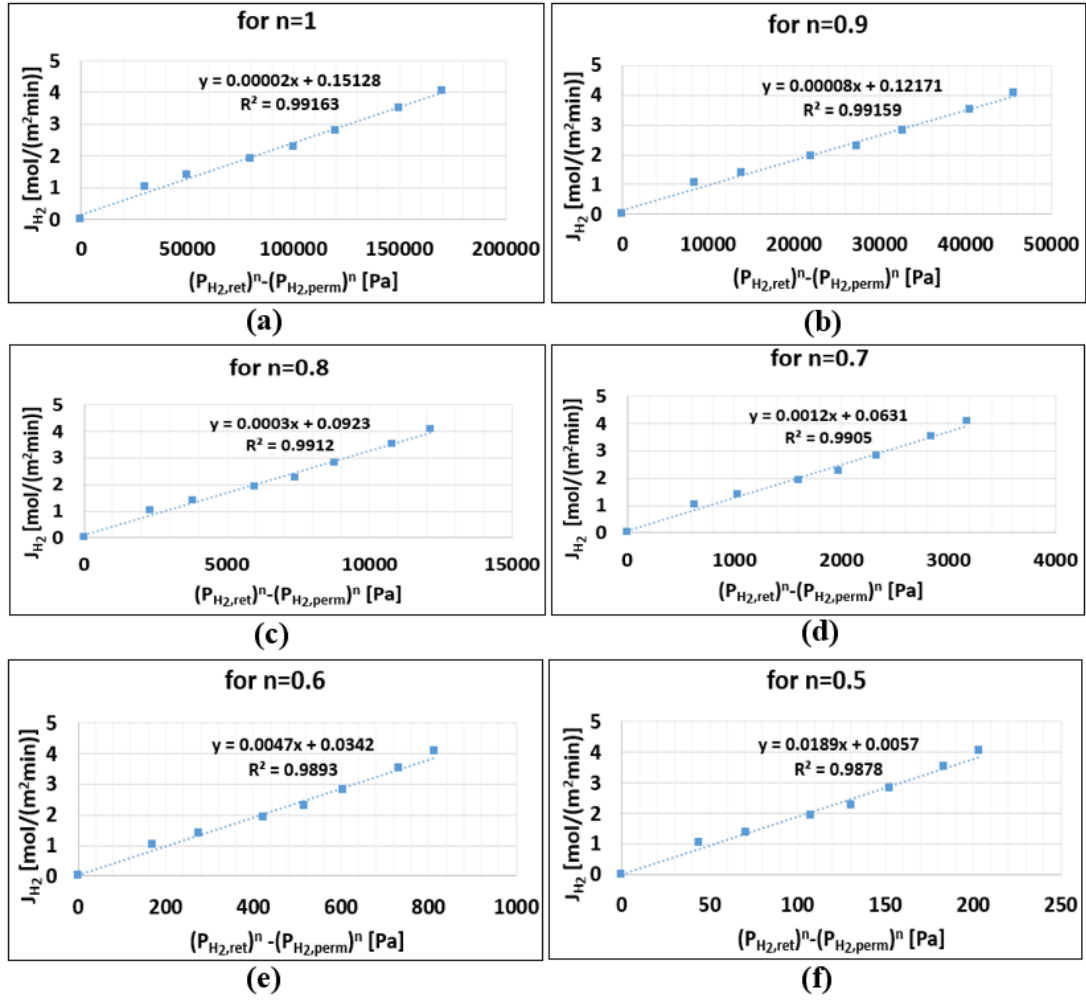


Figure 3.9 Variation of hydrogen flux according to different n values; (a) $n=1$, (b) $n=0.9$, (c) $n=0.8$, (d) $n=0.7$, (e) $n=0.6$, and (f) $n=0.5$

If n is higher than 0.5, the surface effects play an important role in the permeation. This means that the hydrogen flux permeating through the membrane depends not only on the Sievet-Fick law, but also on other mechanisms (Knudsen or Hagen-Poiseuille). In Figure 3.9, the regression coefficients are found as 0.99163, 0.99159, 0.9912, 0.9905, 0.9893 and 0.9878 for 1, 0.9, 0.8, 0.7, 0.6, and 0.5 n values, respectively. The situation where the regression coefficient is closest to 100% is when the n value is equal to 1. The n value being equal to 1 shows that the surface controls are more dominant than diffusion, thus, the Knudsen diffusion mechanism is the most effective mechanism. Another reason for this can be explained that it is caused by defects in the membrane caused by the effect of temperature.

CHAPTER FOUR

MATHEMATICAL MODELING

4.1 Introduction

Mathematical modeling is a method used to predict the system behavior for the dynamic or steady-state mode and can guide in the selection of the operating and design conditions of a high-performance MR. In recent years, several studies have focused on the mathematical modeling of a membrane reactor for different fuels and different approaches to better understanding of the change of mass and energy inside the MR that cannot be easily measured by experimental methods. These models provide more insights compared to experimental studies in the design and optimization of the MRs. According to the findings of the literature survey conducted, the non-detailed some 1-D models of a MR that generally produces hydrogen from methane have been developed. These models have been solved using either numerical or analytical methods. Numerical methods are generally applied to 2-D or 3-D models; whereas analytical methods are generally preferred for 1-D models. According to the findings of the literature survey conducted, limited 2-D and 3-D MR modeling studies have been found. In 2-D models, generally, for the reaction side, the mass and energy balance equations were examined as two-dimensionally, and the momentum balance equations were examined as one-dimensionally. However, the mass and energy balance equations in the permeation side were written with the assumption that they only change through the axial direction. According to the authors' knowledge, no studies on the 3-D modeling of a MR for hydrogen production from methane exist in the literature. However, in the literature, some studies on the 3-D modeling of MRs that produce hydrogen from different chemical reactions, such as methanol steam reforming, water gas shift, ethanol steam reforming, are found.

In Section 4.2, the detailed modeling equations including the mass and energy balance, the reaction kinetics equations, and the hydrogen flux equation are given to

use in the 1-D membrane reactor models. In addition, the discretization of mass and energy balance equations is presented in detail. In Section 4.3, the modeling equations including mass, energy, and exergy balance equations are given for all components in the model of the integrated membrane reactor and CO₂ capture system. In addition, the calculations of the performance variables of the integrated system are presented. In Section 4.4, the 2-D modeling equations are shown according to the four different physics found in the COMSOL Multiphysics software.

4.2 One-Dimensional Model of a Membrane Reactor

Figure 4.1 shows the schematic of a membrane reactor. In this model, the finite difference method was used for the discretization of mass and energy balance equations. This membrane reactor consists of two concentric tubes. Figure 4.2 shows the inner and outer diameters of the tube and shell sides. In this section, the modeling equations are discretized for the reaction side (shell side) and the permeation side (tube side). In the reaction side, steam reforming reactions occur and hydrogen is produced. The portion of the produced hydrogen passes through the hydrogen perm-selective membrane from the reaction side to the permeation side, while the other gases (retentate gas) that do not pass through the membrane exit from the outlet of reaction side. In the permeation side, the passed hydrogen is swept by the sweep gas that is the inert gas such as nitrogen, and the permeate gas including hydrogen and nitrogen exits from the outlet of the permeation side. The sweep gas should be chosen different from the produced species in the reaction side to avoid the back permeation from the permeation side to the reaction side. The sweep gas provides to increase the driving force and to reduce the partial pressure of the permeating species (Barbieri, 2015).

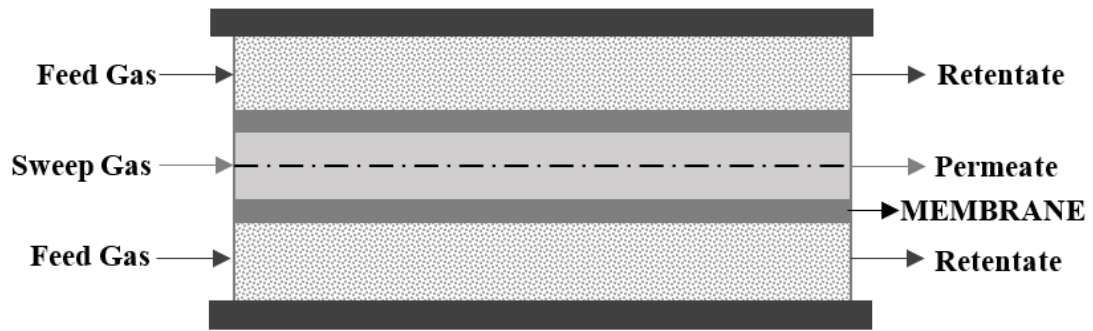


Figure 4.1 The schematic of the membrane reactor in which the reaction side is the shell side, whereas the permeation side is the tube side.

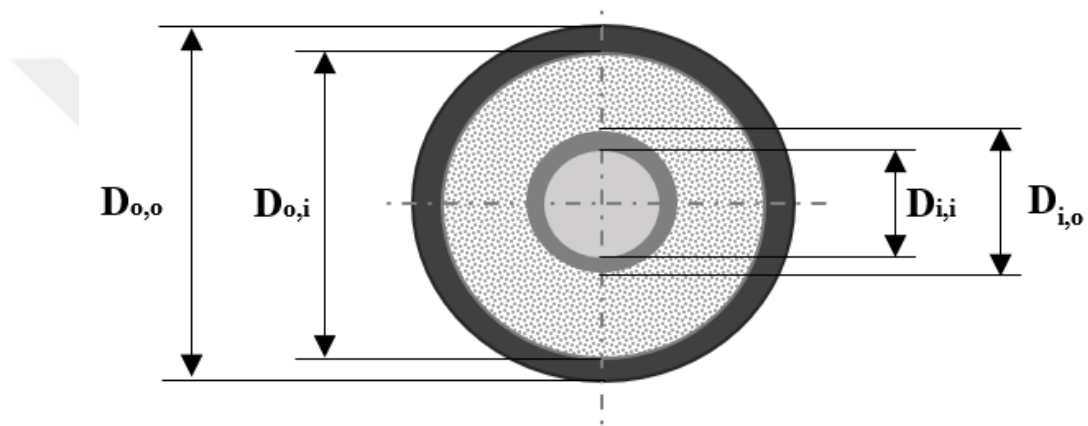


Figure 4.2 Inner and outer diameters of the tube and shell sides

4.2.1 Reaction Kinetics

Hydrogen can be produced by several reforming processes (e.g., steam reforming, partial oxidation reforming, dry reforming). Generally, the steam reforming processes are widely used to produce hydrogen in the industrial applications since it can be a more feasible solution if appropriate conditions are selected compared with the other reforming processes. In addition, this technology is better known and controlled. The detailed information was given in Section 2.5. The chemical reactions in steam-methane reforming processes are given in Eqs. (2.16)-(2.18). The reaction rates for the steam-methane reforming chemical reactions given in Eqs. (2.16)-(2.18) are used (Xu and Froment, 1989):

$$R_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \left[P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq,1}} \right] / (P_{H_2}^{2.5} \cdot DEN^2) \quad (4.1)$$

$$R_2 = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) \left[P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{eq,2}} \right] / (P_{H_2} \cdot DEN^2) \quad (4.2)$$

$$R_3 = k_{0,3} \exp\left(\frac{-E_3}{RT}\right) \left[P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eq,3}} \right] / (P_{H_2}^{3.5} \cdot DEN^2) \quad (4.3)$$

where $k_{0,i}$, $K_{eq,i}$ and E_i are pre-exponential factor, equilibrium constant, and activation energy for i reaction, respectively, given in Table 4.1. P_j is the partial pressure of each species (j : CH₄, CO, H₂, CO₂, H₂O). Finally, DEN is the adsorption of reacting species to active catalyst domains and is calculated as follows:

$$DEN = 1 + K_{CH_4} P_{CH_4} + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}} \quad (4.4)$$

where K_j is the adsorption constant of j species on the catalyst surface and is calculated using Van't Hoff equation, given in Table 4.2 (Xu and Froment, 1989).

$$K_j = K_{j,0} \cdot \exp\left(\frac{-\Delta \bar{h}_i}{RT}\right) \quad (4.5)$$

Table 4.1 The parameters of reaction kinetics and the equilibrium constants (Xu and Froment, 1989)

Reaction No., i	Pre-exponential factor, $k_{0,i}$ (kmol/(kg _{cat} -h))	Activation energy, E_i (kJ/kmol)	Equilibrium constant, $K_{eq,i}$
1	4.21×10^{15} (bar ^{0.5})	240,100	$\exp((-26830/T_{ret}) + 30.114)$ (bar ²)
2	1.95×10^6 (-)	67,130	$\exp((4400/T_{ret}) - 4.036)$ (-)
3	1.02×10^{15} (bar ^{0.5})	243,900	$K_{eq,1} \times K_{eq,2}$ (bar ²)

Table 4.2 Constants in Van't Hoff equation (Xu and Froment, 1989)

Species	Pre-exponential factor, $K_{j,0}$	Adsorption Specific Enthalpy, $\Delta \bar{h}_i$ (kJ/kmol)
CH ₄	6.65×10^{-4} (bar ⁻¹)	-38280
CO	8.23×10^{-5} (bar ⁻¹)	-70650
H ₂	6.12×10^{-9} (bar ⁻¹)	-82900
H ₂ O	1.77×10^5 (bar ⁰)	88680

4.2.2 Conservation of Mass

In the reaction side, the feed gas is reacted with the water and the hydrogen is produced. This hydrogen passes through the Pd-based hydrogen selective membrane to the permeation side. The reaction side is the shell side; while the permeation side is the tube side. Figure 4.3 shows the control volumes of the reaction and the permeation sides for the discretization of the mass balance equations.

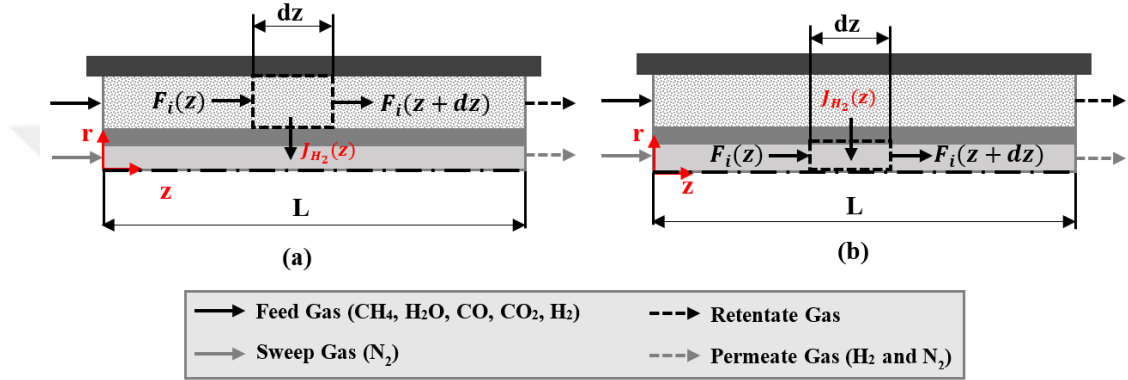


Figure 4.3 Control volumes for mass of (a) reaction and (b) permeation sides

4.2.2.1 Reaction Side

The mass conservation for reaction side can be written as follows:

$$\frac{dF_j^{ret}}{dz} = \rho_b A_c \sum_{i=1}^3 \vartheta_{i,j} R_j \quad (j = CH_4, CO, CO_2, H_2O) \quad (4.6)$$

$$\frac{dF_j^{ret}}{dz} = \rho_b A_c \sum_{i=1}^3 \vartheta_{i,j} R_j - J_{H_2} (2\pi r_{i,o}) \quad (j = H_2) \quad (4.7)$$

where F_j is the molar flow rate of each species (CH_4 , H_2O , CO_2 , CO , H_2 , N_2), dz is the differential length of the reactor, ρ_b is the bed density, A_c is the cross-sectional area, $\vartheta_{i,j}$ is the stoichiometric ratio of the component j in the reaction i , R_j is the reaction rate, i is the reaction number (1, 2, 3), J_{H_2} is the hydrogen flux through the membrane, and r is the radius of the membrane.

4.2.2.2 Permeation Side

The mass conservation for permeation side can be written as follows:

$$\frac{dF_{H_2}^{perm}}{dz} = J_{H_2}(2\pi r_{i,o}) \quad (4.8)$$

$$\frac{dF_{N_2}^{perm}}{dz} = 0 \quad (4.9)$$

The hydrogen flux passing through the membrane with the Sievert Law is calculated by the following equation:

$$J_{H_2} = \frac{B_{H_2}}{\delta} \left(P_{H_2,ret}^{0.5} - P_{H_2,perm}^{0.5} \right) \quad (4.10)$$

where B_{H_2} is the hydrogen permeability (Eq. (4.10)), δ is the thickness of the membrane, $P_{H_2,ret}$ and $P_{H_2,perm}$ are the partial pressure of hydrogen in reaction and permeation sides.

$$B_{H_2} = B_{H_2}^0 \cdot \exp\left(\frac{-E_m}{RT}\right) \quad (4.11)$$

where E_m is the activation energy for permeability, T is temperature, and R is the universal gas constant.

4.2.3 Conservation of Energy

Figure 4.4 shows the schematic of temperatures in the reaction and the permeation sides to calculate the energy balance equations. The wall temperature is constant. The flow type is co-current flow.

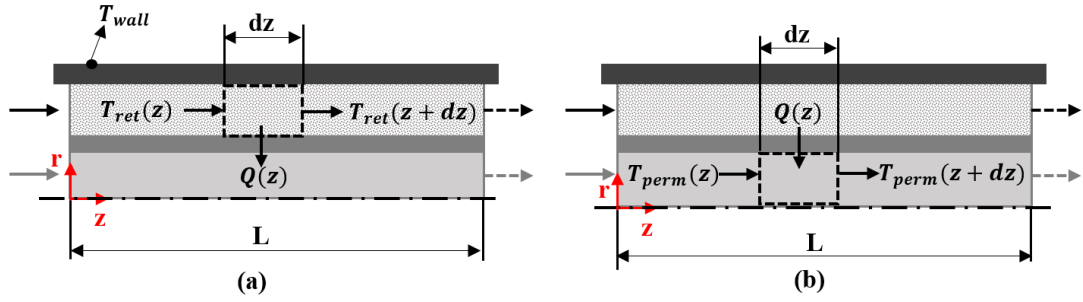


Figure 4.4 Control volumes for energy of (a) reaction and (b) permeation sides

The dynamic viscosity and the thermal conductivity of mixture ideal gases in the reaction and permeation sides are calculated using Wilke's Law (Wilke, 1950) as follows:

$$\mu_{mixture} = \sum_{i=1}^{ns} \frac{\mu_i}{1 + \frac{1}{y_i} \sum_{j=1; j \neq i}^{ns} y_j \varphi_{i,j,\mu}} \quad (4.12)$$

$$\varphi_{i,j,\mu} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (4.13)$$

$$k_{mixture} = \sum_{i=1}^{ns} \frac{k_i}{1 + \frac{1}{y_i} \sum_{j=1; j \neq i}^{ns} y_j \varphi_{i,j,k}} \quad (4.14)$$

$$\varphi_{i,j,k} = \frac{1}{\sqrt{8}} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{k_i}{k_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (4.15)$$

Specific heat capacity ($c_{p,mixture}$) and Prandtl number ($Pr_{mixture}$) of mixture ideal gases are calculated as follows:

$$c_{p,mixture} = \sum y_i c_{p,i} \quad (4.16)$$

$$Pr_{mixture} = \sum y_i Pr_i \quad (4.17)$$

where i and j are each species type (CH₄, H₂O, CO₂, CO, H₂, N₂).

Mass flow rates of the mixture ideal gases for the reaction and permeation sides are calculated as follows:

$$\dot{m}_{ret} = F_{total,ret} MW_{ret} \quad (4.18)$$

$$\dot{m}_{perm} = F_{total,perm} MW_{perm} \quad (4.19)$$

Reynolds numbers for the reaction and permeation sides are calculated as follows:

$$Re_{ret} = \frac{4 \cdot \dot{m}_{ret}}{\mu_{ret} \cdot \pi \cdot Dh_{shell}} \quad (4.20)$$

$$Re_{perm} = \frac{4 \cdot \dot{m}_{perm}}{\mu_{perm} \cdot \pi \cdot Dh_{tube}} \quad (4.21)$$

where F is the molar flow rate, MW is the molecular weight, and Dh is the hydraulic diameter.

When the Reynolds Number is smaller than 2300 and the Prandtl number is smaller than 0.6, Nusselt number is equal to 3.66 for the constant temperature in the circular tube. Therefore, the convective heat transfer coefficients of the reaction and the permeation sides are calculated as follows:

$$h_{ret} = \frac{Nu_{ret} k_{ret}}{Dh_{shell}} \quad (4.22)$$

$$h_{perm} = \frac{Nu_{perm} k_{perm}}{Dh_{tube}} \quad (4.23)$$

In this model, the energy conservation for reaction (Eq. (4.24)) and permeation (Eq. (4.25)) sides can be written as follows:

$$\sum_{i=1}^5 F_i C_{p,i} \frac{dT_{ret}}{dz} = \rho A_c \sum_{j=1}^3 \vartheta_{i,j} R_j (-\Delta H_j) + 2\pi [r_{o,o} U_{shell} (T_{wall} - T_{ret}) - r_{i,o} U_{tube} (T_{ret} - T_{perm})] \quad (4.24)$$

$$\sum_{i=1}^2 F_i C_{p,i} \frac{dT_{perm}}{dz} = 2\pi r_{i,o} U_{tube} (T_{ret} - T_{perm}) \quad (4.25)$$

where $C_{p,i}$ is the specific heat constant of each i species, ΔH_j is the enthalpy of j reaction, U is the heat transfer coefficient for tube and shell sides, and T_{wall} is the wall temperature.

4.2.4 Performance of Membrane Reactor

The performance of the MR is evaluated using the methane conversion and the hydrogen recovery. Methane conversion and hydrogen recovery are defined as the following equations:

$$X_{CH_4} = \frac{(F_{CH_4,in} - F_{CH_4,out})}{F_{CH_4,in}} \quad (4.26)$$

$$Recovery_{H_2} = \frac{(F_{H_2,out}^{perm})}{F_{H_2,out}^{perm} + F_{H_2,out}^{ret}} \quad (4.27)$$

4.2.5 Discretization of Mass and Energy Balance Equations

In this one-dimensional model of the membrane reactor, the equations of reaction kinetics, mass balance equations, and energy balance equations are coupled with the appropriate conditions. Reaction kinetics parameters are based on energy balance equations due to the changing temperatures for reaction and permeation sides. Therefore, the mass balance equations also are based on both reaction kinetics and energy balance equations. All of these equations are discretized using the forward finite difference method in z-direction and solved by the MATLAB program. The discretization of mass and energy balance equations is given for reaction and permeation sides as follows:

$$\frac{F_{CH_4}^{ret}(k+1) - F_{CH_4}^{ret}(k)}{Dz} = \rho_b A_c (-R_1(k) - R_3(k)) \quad (4.28)$$

$$\frac{F_{CO_2}^{ret}(k+1) - F_{CO_2}^{ret}(k)}{Dz} = \rho_b A_c (R_2(k) + R_3(k)) \quad (4.29)$$

$$\frac{F_{H_2O}^{ret}(k+1) - F_{H_2O}^{ret}(k)}{Dz} = \rho_b A_c (-R_1(k) - R_2(k) - 3R_3(k)) \quad (4.30)$$

$$\frac{F_{CO}^{ret}(k+1) - F_{CO}^{ret}(k)}{Dz} = \rho_b A_c (R_1(k) - R_2(k)) \quad (4.31)$$

$$\frac{F_{H_2}^{ret}(k+1) - F_{H_2}^{ret}(k)}{Dz} = \rho_b A_c (3R_1(k) + R_2(k) + 4R_3(k)) - J_{H_2}(k)(2\pi r_{i,o}) \quad (4.32)$$

$$\frac{F_{H_2}^{perm}(k+1) - F_{H_2}^{perm}(zk)}{Dz} = J_{H_2}(k)(2\pi r_{i,o}) \quad (4.33)$$

$$\frac{F_{N_2}^{perm}(k+1) - F_{N_2}^{perm}(k)}{Dz} = 0 \quad (4.34)$$

Some simplifications (AA, BB, and CC) are shown to solve the energy balance equation of reaction side in Eq. (4.24).

$$AA(k) = \rho A_c \sum_{j=1}^3 \vartheta_{i,j} R_j (-\Delta H_j) \quad (4.35)$$

$$AA(k) = \rho A_c [AA_{CH_4}(k) + AA_{H_2O}(k) + AA_{CO_2}(k) + AA_{H_2}(k) + AA_{CO}(k)] \quad (4.36)$$

$$AA_{CH_4}(k) = -R_1(k) \cdot (-\Delta H_1) - R_3(k) \cdot (-\Delta H_3) \quad (4.37)$$

$$AA_{H_2O}(k) = -R_1(k) \cdot (-\Delta H_1) - R_2(k) \cdot (-\Delta H_2) - 2 \cdot R_3(k) \cdot (-\Delta H_3) \quad (4.38)$$

$$AA_{CO_2}(k) = +R_2(k) \cdot (-\Delta H_2) + R_3(k) \cdot (-\Delta H_3) \quad (4.39)$$

$$AA_{H_2}(k) = 3 \cdot R_1(k) \cdot (-\Delta H_1) + R_2(k) \cdot (-\Delta H_2) + 4 \cdot R_3(k) \cdot (-\Delta H_3) \quad (4.40)$$

$$AA_{CO}(k) = +R_1(k) \cdot (-\Delta H_1) - R_2(k) \cdot (-\Delta H_2) \quad (4.41)$$

$$BB(k) = \sum_{i=1}^5 F_i C_{p,i} \quad (4.42)$$

$$BB(k) = [F_{CH_4,r}(k) \cdot C_{p,CH_4}(k)] + [F_{H_2O,r}(k) \cdot C_{p,H_2O}(k)] + [F_{CO_2,r}(k) \cdot C_{p,CO_2}(k)] + [F_{H_2,r}(k) \cdot C_{p,H_2}(k)] + [F_{CO,r}(k) \cdot C_{p,CO}(k)] \quad (4.43)$$

$$CC(k) = 2\pi [r_{o,o} U_{shell}(k) \cdot (T_{wall} - T_{ret}(k)) - r_{i,o} U_{tube}(k) \cdot (T_{ret}(k) - T_{perm}(k))] \quad (4.44)$$

Therefore, when Eq. (4.24) is discretized and these simplifications are added, Eq. (4.24) can be rewritten as follows:

$$\frac{T_{ret}(k+1) - T_{ret}(k)}{Dz} = \frac{AA(k)}{BB(k)} + \frac{CC(k)}{BB(k)} \quad (4.45)$$

Similarly, some simplifications (DD and EE) are shown to solve the energy balance equation of permeation side in Eq. (4.25).

$$DD(k) = \sum_{i=1}^2 F_i C_{p,i} = [F_{H_2,p}(k) \cdot C_{p,H_2}(k)] + [F_{N_2,p}(k) \cdot C_{p,N_2}(k)] \quad (4.46)$$

$$EE(k) = 2\pi r_{i,o} U_{tube}(k) \cdot (T_{ret}(k) - T_{perm}(k)) \quad (4.47)$$

Therefore, when Eq. (4.25) is discretized and these simplifications are added, Eq. (4.25) can be rewritten as follows:

$$\frac{T_{perm}(k+1) - T_{perm}(k)}{\Delta z} = \frac{EE(k)}{DD(k)} \quad (4.48)$$

4.3 Modeling of an Integrated Membrane Reactor and CO₂ Capture System to Generate Decarbonized Hydrogen

In this section, component-based modeling equations including mass and energy balances and exergy analysis of the integrated system are presented in detail. Firstly, a 1-D mathematical model of a MR was developed and the molar flow rate distribution of each species through the reactor length in both reaction and permeation side were presented. In addition, the performance parameters of the MR (methane conversion and hydrogen recovery) were compared with the results of the reference study (Alavi et al., 2017). Then, the changes in methane conversion and hydrogen recovery through the reactor length were investigated. In this study, the membrane housed in the MR is assumed as fully H₂ perm-selective, and thus it is able to separate high-grade hydrogen (purity > 99.9999%). The membrane permeability properties were taken according to a dense Pd-Ag (23 wt% of Ag) membrane (Iulianelli et al., 2010). Inlet operating conditions of the MR (e.g., molar flow rates, temperatures, and pressures) were taken from the study of Alavi et al. (2017). Then, the validated MR model was coupled with the models of different plant components (compressor, boiler, burner, pump, blower, and two mixers) and the CO₂ capture system. Finally, the energy and exergy analyses of the integrated system were conducted in detail. The effect the operating temperature on the MR performance in terms of hydrogen production molar flow rate, the amount of the captured CO₂, the methane conversion, hydrogen yield, CO₂ yield, and thermal efficiency was carefully evaluated. Figure 4.5 shows the schematic of the integrated system including a MR, a CO₂ capture system, and the other components.

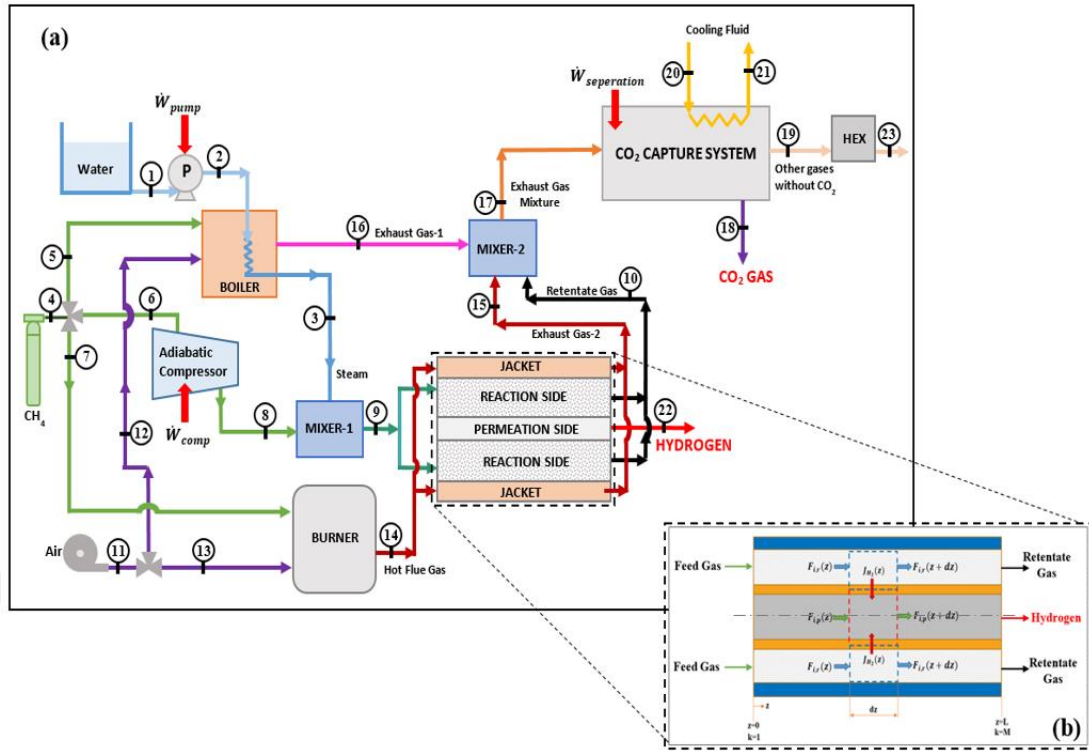


Figure 4.5 a) Schematic of the integrated system including a MR, a CO₂ capture stage, and the other components; b) Schematic of the MR and the finite difference element used for deriving the conservation equations

As shown in Figure 4.5, methane is fed to the system from State 4, and the methane line is separated into three lines (States 5, 6, 7) by a three ways valve. These methane lines enter the MR (State 6), the burner (State 7), and the boiler (State 5). In the MR, the feed gas including methane and water is fed to the inlet of the reaction side, and the steam methane reforming, water gas shift, and direct steam methane reforming reactions occur in the catalyst site. Thus, hydrogen is produced on the reaction side and then it is removed for permeation through a hydrogen fully perm-selective membrane, to be collected in the permeation side. The permeated hydrogen leaves from State 22, and considering its purity ($> 99.9999\%$), it can be used in low temperature PEM fuel cell applications.

A burner is used to provide the required heat for the endothermic chemical reactions realized on the reaction side of the MR. In the burner, methane and air are burned, and the hot flue gas is produced and fed to the jacket of the MR, to provide the energy inputs required for carrying out the endothermic reaction of steam reforming of

methane. A boiler is used to transform water into steam, which is fed to the MR. The exhaust gases, coming out from the MR, the burner and the boiler, including hydrogen, methane, carbon monoxide, carbon dioxide, nitrogen, and water, are mixed in the Mixer-2. The latter is combined with the CO₂ capture system to separate CO₂ from the other exhaust gases. Then, the analysis about the end use of the captured CO₂ was out of the scope of this work, even though much often it could be directed to power-to-gas systems. The other gases except for CO₂ are sent heat exchanger since their temperature is very high and then the absorbed heat is used to provide heat to any application.

4.3.1 1-D Membrane Reactor Modeling

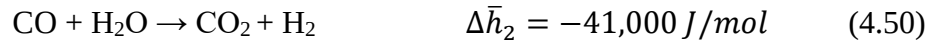
Figure 4.5-(b) shows the schematic of the MR and the finite difference element. Here, 'dz' represents the differential length in flow direction used for deriving the mass and energy conservation equations. In this 1-D model, the temperature changes are assumed only in the axial direction and the diffusion through the axial direction is ignored. The reaction takes place in the annulus of the MR, while hydrogen is recovered in the membrane core that is also the permeation side. The feed gas enters the reaction side, where the steam methane reforming reaction occurs in the presence of a Ni-based reforming catalyst. Part of the produced hydrogen permeates through the hydrogen perm-selective membrane to be collected in the permeation side, depending on the hydrogen permeation driving force applied. The retentate stream leaves the MR and it is rich in unconverted methane, carbon dioxide, carbon monoxide, steam, and residual hydrogen. Table 4.3 summarizes the operating and geometric parameters used in this model.

Table 4.3 The operating and geometric parameters used in the MR model

Parameter	Value	Parameter	Value
Reactor length, L	1 m	Inlet pressure of the reaction side, $P_{ret,in}$	9 bar
External tube external radius, $r_{o,o}$	0.0875 m	Inlet pressure of the permeation side, $P_{perm,in}$	1 bar
External tube internal radius, $r_{o,i}$	0.0775 m	Inlet molar flow rate of CH ₄ , $F_{CH_4,in}$	0.15 kmol/h
Internal tube external radius, $r_{i,o}$	0.045 m	Inlet mole fraction of H ₂ O, X_{H_2O}	0.7258
Internal tube internal radius, $r_{i,i}$	0.035 m	Inlet mole fraction of CO ₂ , X_{CO_2}	0.0113
Bed density, ρ	260 kg/m ³	Inlet mole fraction of CO, X_{CO}	0.0023
Inlet temperature of the reaction side, $T_{ret,in}$	773 K	Inlet mole fraction of H ₂ , X_{H_2}	0.034
Inlet temperature of the permeation side, $T_{perm,in}$	773 K	Sweep Ratio	4

4.3.1.1 Reaction Kinetics

The reaction mechanism taking place during steam-methane reforming process is reported below:



The reaction rates for the steam-methane reforming reactions (Eqs. (4.49)-(4.51)) are calculated as follows:

$$R_1 = k_{0,1} \exp\left(\frac{-E_1}{RT}\right) \left[p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_{eq,1}} \right] / (p_{H_2}^{2.5} \cdot DEN^2) \quad (4.52)$$

$$R_2 = k_{0,2} \exp\left(\frac{-E_2}{RT}\right) \left[p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_{eq,2}} \right] / (p_{H_2} \cdot DEN^2) \quad (4.53)$$

$$R_3 = k_{0,3} \exp\left(\frac{-E_3}{RT}\right) \left[p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_{eq,3}} \right] / (p_{H_2}^{3.5} \cdot DEN^2) \quad (4.54)$$

where $k_{0,i}$, $K_{eq,i}$ and E_i are the pre-exponential factor, equilibrium constant, and activation energy for i^{th} reaction, respectively, as reported in Table 4.1. p_j is the partial

pressure of each species (j: CH₄, CO, H₂, CO₂, H₂O). Finally, DEN is the adsorption factor of reacting species to active catalyst domains and calculated as follows:

$$DEN = 1 + K_{CH_4}p_{CH_4} + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}} \quad (4.55)$$

where K_j is the adsorption constant of j species on the catalyst surface and calculated using Van't Hoff equation, as given in Table 4.2.

$$K_j = K_{j,0} \cdot \exp\left(\frac{-\Delta\bar{h}_i}{\bar{R}T}\right) \quad (4.56)$$

where $K_{j,0}$ is the pre-exponential factor. $\Delta\bar{h}_i$ is the adsorption specific enthalpy of species i. $\bar{R}$ and T are the universal gas constant and temperature, respectively.

4.3.1.2 Conservation of Mass

The mass conservation for the reaction (Eqs. (4.57) and (4.58)) and permeation (Eq. (4.59)) sides can be written as follows:

$$\frac{d\dot{n}_j^{ret}}{dz} = \rho_b A_c \sum_{i=1}^3 \vartheta_{i,j} R_j \quad (j = CH_4, CO, CO_2, H_2O) \quad (4.57)$$

$$\frac{d\dot{n}_j^{ret}}{dz} = \rho_b A_c \sum_{i=1}^3 \vartheta_{i,j} R_j - J_{H_2}(2\pi r_{i,o}) \quad (j = H_2) \quad (4.58)$$

$$\frac{d\dot{n}_{H_2}^{perm}}{dz} = J_{H_2}(2\pi r_{i,o}) \quad (4.59)$$

where $\dot{n}_j$ is the molar flow rate of each species (CH₄, H₂O, CO₂, CO, H₂), dz is the differential length of the reactor, ρ_b is the bed density, A_c is the cross-sectional area, $\vartheta_{i,j}$ is the stoichiometric ratio of the component j in the reaction i, R_j is the reaction rate, i is the reaction number (1, 2, 3), J_{H_2} is the hydrogen flux through the membrane, and r is the radius of the membrane. The hydrogen flux passing through the membrane may be calculated by using the Sieverts-Fick Law (Amiri et al., 2020), Eq. (4.60):

$$J_{H_2} = \frac{B_{H_2}}{\delta} (p_{H_2,ret}^{0.5} - p_{H_2,perm}^{0.5}) \quad (4.60)$$

where B_{H_2} is the hydrogen permeability (Eq. (4.61)), δ is the thickness of the membrane, $p_{H_2,ret}$ and $p_{H_2,perm}$ are the partial pressure of hydrogen in the reaction and permeation sides, respectively.

$$B_{H_2} = B_{H_2}^0 \cdot \exp\left(\frac{-E_m}{RT}\right) \quad (4.61)$$

where E_m is the activation energy for permeability, T is temperature, and $\bar{R}$ is the universal gas constant.

4.3.1.3 Conservation of Energy

In this model, the energy conservation for reaction (Eq. (4.62)) and permeation (Eq. (4.63)) sides can be written as follows:

$$\sum_{i=1}^5 \dot{n}_i C_{p,i} \frac{dT_{ret}}{dz} = \rho A_c \sum_{j=1}^3 \vartheta_{i,j} R_j (-\Delta H_j) + 2\pi [r_{o,o} U_{shell} (T_{wall} - T_{ret}) - r_{i,o} U_{tube} (T_{ret} - T_{perm})] \quad (4.62)$$

$$\sum_{i=1}^2 \dot{n}_i C_{p,i} \frac{dT_{perm}}{dz} = 2\pi r_{i,o} U_{tube} (T_{ret} - T_{perm}) \quad (4.63)$$

where $C_{p,i}$ is the specific heat constant of each i species, ΔH_j is the enthalpy of j reaction, U is the overall heat transfer coefficient for tube and shell sides, and T_{wall} is the wall temperature (taken as 950 K in this study).

4.3.1.4 Performance of the MR

The performance of the MR is here defined in terms of methane conversion and hydrogen recovery. The equations of methane conversion (Eq. (4.64)) and hydrogen recovery (Eq. (4.65)) in the MR are shown below:

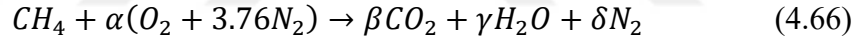
$$X_{CH_4} = \left(\frac{\dot{n}_{CH_4,in} - \dot{n}_{CH_4,out}}{\dot{n}_{CH_4,in}} \right) \quad (4.64)$$

$$Recovery_{H_2} = \left(\frac{\dot{n}_{H_2,out}^{perm}}{\dot{n}_{H_2,out}^{perm} + \dot{n}_{H_2,out}^{ret}} \right) \quad (4.65)$$

where $\dot{n}_{CH_4,in}$ and $\dot{n}_{CH_4,out}$ are defined as the inlet molar flow rate of methane in feed gas and the outlet molar flow rate of methane in the retentate stream. $\dot{n}_{H_2,out}^{perm}$ and $\dot{n}_{H_2,out}^{ret}$ are defined as the outlet molar flow rate of hydrogen in the permeate stream and the outlet molar flow rate of hydrogen in the retentate stream.

4.3.2 Burner and Boiler

In the burner and the reaction side of the boiler, dry air (O₂ and N₂) and methane (CH₄) are considered to burn in complete combustion to produce hot flue gases. The general chemical reactions occurring in the burner and the boiler are shown in Eq (4.66). For both burner and boiler, C, H, O, and N atom balances and the energy balance are solved, and then the molar flow rates of the exhaust gases ($\dot{n}_{14}$ and $\dot{n}_{16}$) are calculated.



4.3.3 CO₂ Capture System

CO₂ capture systems can separate approximately 90% percent of the total CO₂ present in the exhaust gases produced from different plants (Iulianelli et al., 2016c). Captured CO₂ can be used in the power-to-gas technologies or stored. In this study, two exhaust gases coming out from the burner and boiler and the MR retentate gas are mixed in the Mixer-2. The mixed gases enter the CO₂ capture system, and it is assumed in this study that CO₂ is fully captured. In this system, the temperatures and pressures are kept constant for both the inlet and outlet streams. Thus, the minimum required work (J/mol of mixture) for the separation of CO₂ from the mixture gas can be calculated as follows:

$$w_{min,sep} = \bar{R}T \left(X_{CO_2} \ln(X_{CO_2}) + X_{rest} \ln(X_{rest}) \right) \quad (4.67)$$

$$X_{CO_2} = \frac{\dot{n}_{17,CO_2}}{\dot{n}_{17}} \quad (4.68)$$

$$X_{rest} = 1 - X_{CO_2} \quad (4.69)$$

where $\dot{n}_{17}$ can be calculated as the sum of molar flow rates of State 10, State 15, and State 16. The minimum total work (J/s) required to separate CO₂ from the mixture can be calculated as in the following:

$$\dot{W}_{min,sep} = w_{min,sep} \times \dot{n}_{17} \quad (4.70)$$

The power required to separate CO₂ can be calculated from Eq. (4.71). In this study, the second law efficiency is assumed as 0.25 (Ghoniem, 2021).

$$\dot{W}_{sep} = \frac{\dot{W}_{min,sep}}{\eta_{second,law}} \quad (4.71)$$

4.3.4 Mass and Energy Rate Balance Equations for the Integrated System

Mass and energy rate balance equations at steady-state conditions are given in Eqs. (4.72) and (4.73). These equations are applied to all components used in the system-level model.

$$\sum \dot{n}_i MW_i - \sum \dot{n}_e MW_e = 0 \quad (4.72)$$

$$\dot{Q}_{cv} - \dot{W}_{cv} + \sum \dot{n}_i \cdot \left(\bar{h}_i + \frac{V_i^2}{2} + gz_i \right) - \sum \dot{n}_e \cdot \left(\bar{h}_e + \frac{V_e^2}{2} + gz_e \right) = 0 \quad (4.73)$$

where $\dot{n}$ and MW are defined as molar flow rate (mol/s) and molecular weight (g/mole). The subscripts, i and e, are the abbreviation of inlet and exit, respectively. $\bar{h}$, $\dot{Q}$, and $\dot{W}$ are defined as the specific enthalpy (J/mole), the rate of heat transfer (J/s), and the rate of work transfer (J/s), respectively.

4.3.5 Exergy Analysis of the Integrated System

In this section, the exergy balance equations for the integrated system are given. The total flow exergy includes the physical exergy ($\overline{ex}_i^{PH}$) and the chemical exergy ($\overline{ex}_i^{CH}$), when the kinetic and potential exergies are ignored. The total exergy of the stream i ($\overline{ex}_i$) can be calculated as reported below:

$$\overline{ex}_i = \overline{ex}_i^{PH} + \overline{ex}_i^{CH} \quad (4.74)$$

Physical exergy is defined as the maximum useful work achieved when the system reaches restricted dead state, where the system is at thermal and mechanical equilibrium with the environment (Catrini et al., 2018). The physical exergy can be calculated on molar basis using Eq. (4.75) if the kinetic and potential exergy effects are negligible. Chemical exergy is defined as the maximum useful work of a system when the system is brought from restricted dead state to dead state, where the system is also in chemical equilibrium with the environment (Catrini et al., 2018). Chemical exergy for an ideal gas mixture is calculated on a molar basis using Eq. (4.76).

$$\overline{ex}_i^{PH} = (\bar{h}_i - \bar{h}_0) - T_0 \cdot (\bar{s}_i - \bar{s}_0) \quad (4.75)$$

$$\overline{ex}_i^{CH} = \sum X_j \cdot \overline{ex}_j^{CH} + \bar{R} \cdot T_0 \cdot \sum X_j \cdot \ln(X_j) \quad (4.76)$$

where $\bar{h}$, $\bar{s}$, and X_j are the specific enthalpy, specific entropy, and the mole fraction of the species, respectively. The subscript 0 indicates the value of the property at the dead-state condition (taken as 298.15 K and 101.325 kPa). All thermophysical properties of each species are taken from CoolProp, and then used in MATLAB.

The exergy balance rate equation at the steady-state conditions is shown as follows:

$$\sum_j \dot{E}_{Q,j} - \dot{W}_{cv} + \sum_i \dot{E}x_i - \sum_e \dot{E}x_e - \dot{E}x_D = 0 \quad (4.77)$$

where $\dot{E}_{Q,j}$ is the rate of exergy transfer due to heat transfer (Eq. (4.78)). $\dot{W}_{cv}$ is the rate of exergy transfer due to work. $\dot{E}x_i$ and $\dot{E}x_e$ are the rate of exergy transfers due to the input and output flows (Eqs. (4.79) and (4.80)). $\dot{E}x_D$ is the exergy destruction rate in the control volume.

$$\dot{E}_{Q,j} = \left(1 - \frac{T_0}{T_j}\right) \cdot \dot{Q}_j \quad (4.78)$$

$$\dot{E}x_i = \dot{n}_i \cdot \bar{e}x_i \quad (4.79)$$

$$\dot{E}x_e = \dot{n}_e \cdot \bar{e}x_e \quad (4.80)$$

where $\bar{e}x_i$ and $\bar{e}x_e$ are defined as the specific molar exergy of input and output species. Table 4.4 shows the control volumes, molar rate, energy rate, and the exergy rate balance equations of each component in the integrated system. The ratio between the exergy destruction rate of component i and the exergy rate of the methane supplied to the integrated system (y_D) is calculated as:

$$y_D = \frac{\dot{E}x_{D,i}}{\dot{E}x_{CH_4}} \quad (4.81)$$

4.3.6 Performance Assessment Parameters

The performance of the system is assessed in terms of different efficiency parameters (methane conversion, hydrogen yield, CO₂ yield, and thermal efficiency). The methane conversion of the system ($Conv_{sys_CH_4}$) given in Eq. (4.82) is defined as the ratio of the difference in molar flow rates of methane between the inlet and outlet of the system to the molar flow rate of the methane entering the system. Hydrogen (Eq. (4.83)) and CO₂ (Eq. (4.84)) yields are defined as the ratio of the molar flow rate of the desired product (hydrogen or CO₂) from the system to the molar flow rate of methane entering the system. The thermal efficiency based on LHV of the system ($\eta_{th,LHV}$) and the thermal efficiency based on HHV of the system ($\eta_{th,HHV}$) are defined as the ratio between the summation of the rate of useful heat output (State 19) and the lower heating value/higher heating value of the desired product (State 22) to the lower

heating value/higher heating value of the fuel entering the system, as shown in Eqs. (4.85) and (4.86).

$$Conv_{sys_CH_4} = \frac{\dot{n}_4 - \dot{n}_{19,CH_4}}{\dot{n}_4} \quad (4.82)$$

$$Yield_{H_2} = \frac{\dot{n}_{22}}{\dot{n}_4} \times 100 \quad (4.83)$$

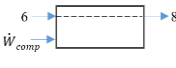
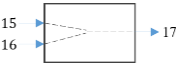
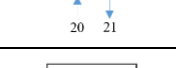
$$Yield_{CO_2} = \frac{\dot{n}_{18}}{\dot{n}_4} \times 100 \quad (4.84)$$

$$\eta_{th,LHV} = \frac{(\dot{n}_{22} \times MW_{H_2} \times LHV_{H_2}) + (\dot{n}_{19}[\bar{h}_{19} - \bar{h}_{23}]) + (\dot{n}_{20}[\bar{h}_{21} - \bar{h}_{20}])}{(\dot{n}_4 \times MW_{CH_4} \times LHV_{CH_4}) + \dot{W}_{total}} \quad (4.85)$$

$$\eta_{th,HHV} = \frac{(\dot{n}_{22} \times MW_{H_2} \times HHV_{H_2}) + (\dot{n}_{19}[\bar{h}_{19} - \bar{h}_{19,0}]) + (\dot{n}_{20}[\bar{h}_{21} - \bar{h}_{20}])}{(\dot{n}_4 \times MW_{CH_4} \times HHV_{CH_4}) + \dot{W}_{total}} \quad (4.86)$$

where $\dot{n}_{22}$, $\dot{n}_4$, $\dot{n}_{18}$, $\dot{n}_{19}$, and $\dot{n}_{20}$ are defined as the molar flow rate of the produced hydrogen from the MR, the molar flow rate of the methane entering the integrated system, the molar flow rate of the captured CO₂, the molar flow rate of the exhaust gases except for CO₂, and the molar flow rate of the cooling water in the CO₂ capture system, respectively. MW , LHV , and HHV are the molecular weight, the lower heating value, and the higher heating value, respectively. $\dot{W}_{total}$ is defined as the total power input into the integrated system and it is calculated as the sum of the power input to the pump ($\dot{W}_{pump}$), the compressor ($\dot{W}_{comp}$), and the separation unit ($\dot{W}_{sep}$).

Table 4.4 Control volume, molar rate, energy rate, and exergy rate balance equations of all components in the integrated system

Components	Control Volume	Mass Rate, Energy Rate, and Exergy Rate Balance Equations
Water Pump		$\dot{m}_1 - \dot{m}_2 = 0$ $\dot{W}_{pump} + \dot{n}_1 \bar{h}_1 - \dot{n}_2 \bar{h}_2 = 0$ $\dot{W}_{pump} + \dot{E}x_1 - \dot{E}x_2 - \dot{E}x_{D,pump} = 0$
Compressor		$\dot{m}_6 - \dot{m}_8 = 0$ $\dot{W}_{comp} + \dot{n}_6 \bar{h}_6 - \dot{n}_8 \bar{h}_8 = 0$ $\dot{W}_{comp} + \dot{E}x_6 - \dot{E}x_8 - \dot{E}x_{D,comp} = 0$
Mixer-1		$\dot{m}_3 - \dot{m}_8 - \dot{m}_9 = 0$ $\dot{n}_3 \bar{h}_3 - \dot{n}_8 \bar{h}_8 - \dot{n}_9 \bar{h}_9 = 0$ $\dot{E}x_3 + \dot{E}x_8 - \dot{E}x_9 - \dot{E}x_{D,mixer-1} = 0$
Mixer-2		$\dot{m}_{15} - \dot{m}_{16} - \dot{m}_{17} = 0$ $\dot{n}_{15} \bar{h}_{15} - \dot{n}_{16} \bar{h}_{16} - \dot{n}_{17} \bar{h}_{17} = 0$ $\dot{E}x_{15} + \dot{E}x_{16} - \dot{E}x_{17} - \dot{E}x_{D,mixer-2} = 0$
Membrane Reactor		$\dot{m}_9 + \dot{m}_{14} - \dot{m}_{10} - \dot{m}_{22} - \dot{m}_{15} = 0$ $\dot{n}_9 \bar{h}_9 - \dot{n}_{10} \bar{h}_{10} - \dot{n}_{22} \bar{h}_{22} + \dot{n}_{14} \bar{h}_{14} - \dot{n}_{15} \bar{h}_{15} = 0$ $\dot{E}x_9 + \dot{E}x_{14} - \dot{E}x_{10} - \dot{E}x_{22} - \dot{E}x_{15} - \dot{E}x_{D,MR} = 0$
Valve-1		$\dot{m}_4 - \dot{m}_5 - \dot{m}_6 - \dot{m}_7 = 0$ $\dot{n}_4 \bar{h}_4 - \dot{n}_5 \bar{h}_5 - \dot{n}_6 \bar{h}_6 - \dot{n}_7 \bar{h}_7 = 0$ $\dot{E}x_4 - \dot{E}x_5 - \dot{E}x_6 - \dot{E}x_7 - \dot{E}x_{D,valve-1} = 0$
Valve-2		$\dot{m}_{11} - \dot{m}_{12} - \dot{m}_{13} = 0$ $\dot{n}_{11} \bar{h}_{11} - \dot{n}_{12} \bar{h}_{12} - \dot{n}_{13} \bar{h}_{13} = 0$ $\dot{E}x_{11} - \dot{E}x_{12} - \dot{E}x_{13} - \dot{E}x_{D,valve-2} = 0$
Burner		$\dot{m}_7 + \dot{m}_{13} + \dot{m}_{10} - \dot{m}_{14} = 0$ $\dot{n}_7 \bar{h}_7 + \dot{n}_{13} \bar{h}_{13} + \dot{n}_{10} \bar{h}_{10} - \dot{n}_{14} \bar{h}_{14} = 0$ $\dot{E}x_7 + \dot{E}x_{13} + \dot{E}x_{10} - \dot{E}x_{14} - \dot{E}x_{D,burner} = 0$
Boiler		$\dot{m}_5 + \dot{m}_{12} + \dot{m}_2 - \dot{m}_{16} - \dot{m}_3 = 0$ $\dot{n}_5 \bar{h}_5 + \dot{n}_{12} \bar{h}_{12} + \dot{n}_2 \bar{h}_2 - \dot{n}_{16} \bar{h}_{16} - \dot{n}_3 \bar{h}_3 = 0$ $\dot{E}x_5 + \dot{E}x_{12} + \dot{E}x_2 - \dot{E}x_{16} - \dot{E}x_3 - \dot{E}x_{D,boiler} = 0$
CO ₂ Capture System		$\dot{m}_{17} + \dot{m}_{20} - \dot{m}_{18} - \dot{m}_{19} - \dot{m}_{21} = 0$ $\dot{W}_{sep} + \dot{n}_{17} \bar{h}_{17} - \dot{n}_{18} \bar{h}_{18} - \dot{n}_{19} \bar{h}_{19} + \dot{n}_{20} \bar{h}_{20} - \dot{n}_{21} \bar{h}_{21} = 0$ $\dot{E}x_{17} + \dot{E}x_{20} - \dot{E}x_{18} - \dot{E}x_{19} - \dot{E}x_{21} - \dot{W}_{sep} - \dot{E}x_Q - \dot{E}x_{D,capt} = 0$
HEX		$\dot{m}_{19} - \dot{m}_{23} = 0$ $\dot{n}_{19} \bar{h}_{19} - \dot{n}_{23} \bar{h}_{23} - \dot{Q} = 0$ $\dot{E}x_{19} - \dot{E}x_{23} - \dot{E}_Q - \dot{E}x_{D,HEX} = 0$

4.4 Two-Dimensional Model of a Membrane Reactor

The aim of the development of the 2-D membrane reactor model is to give more realistic results when compared to the 1-D models. As can be known, 1-D modeling is the most common type of modeling. In this modeling type, the property changes in only one dimension (axial coordinate) are taken into account; therefore, the solution of one-dimensional models is relatively easier than the others. However, the gradients of the concentration and the temperature in the radial coordinate significantly affect the hydrogen flux through membrane and heat transfer (Nalbant Atak et al., 2021).

Therefore, a 2-D modeling method that also includes the radial coordinate may be preferred.

4.4.1 Mass and Energy Balance Equations

2-D model of a membrane reactor includes considerations of mass and heat transfer in the radial and axial directions. The mass balance equations used in the 2-D models are given according to the reaction (Eq. (4.87)) and permeation (Eq. (4.88)) sides. Table 4.5 shows the initial and boundary conditions used in the 2-D mass balance equations for the reaction and permeation sites.

$$\frac{\partial P_i^R}{\partial t} = D_{i,z} \frac{\partial^2 P_i^R}{\partial z^2} + D_{i,r} \frac{\partial^2 P_i^R}{\partial r^2} + RT_R \left(-\frac{\partial F_i^R}{\partial z} + \sum_{j=1}^{N_R} v_{i,j} r_j \right) \quad (4.87)$$

$$\frac{\partial P_i^P}{\partial t} = D_{i,z} \frac{\partial^2 P_i^P}{\partial z^2} + D_{i,r} \frac{\partial^2 P_i^P}{\partial r^2} - RT_P \frac{\partial F_i^P}{\partial z} \quad (4.88)$$

Table 4.5 Initial and boundary conditions for mass balance equations used in 2-D models (Nalbant Atakel et al., 2021)

Side	Conditions	Equations
Reaction Side	Initial Conditions	$P_i^R(z, r) \big _{t=0} = P_i^{R,initial}$
	Boundary Conditions	$P_i^R \big _{z=0} = P_i^{feed}$
		$\frac{\partial P_i^R}{\partial z} \big _{z=L} = 0$
Permeation Side	Initial Conditions	$P_i^P(z, r) \big _{t=0} = P_i^{P,initial}$
	Boundary Conditions	$P_i^P \big _{z=0} = P_i^{sweep}$ (Co-current Flow)
		$P_i^P \big _{z=L} = P_i^{sweep}$ (Counter-current Flow)
		$\frac{\partial P_i^P}{\partial z} \big _{z=L} = 0$

The energy balance equations used in the 2-D models are given according to the reaction (Eq. (4.89)) and permeation (Eq. (4.90)) sides. Table 4.6 shows the initial and boundary conditions used in these energy balance equations for the tube and shell sides.

$$\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{tube}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C p_i \frac{\partial T_{tube}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{tube}}{\partial z^2} \right] + \left[k_r \frac{\partial^2 T_{tube}}{\partial r^2} \right] + \psi \quad (4.89)$$

$$\sum_{i=1}^{N_s} C_i C p_i \frac{\partial T_{an}}{\partial t} = - \left[\sum_{i=1}^{N_s} F_i C p_i \frac{\partial T_{an}}{\partial z} \right] + \left[k_z \frac{\partial^2 T_{an}}{\partial z^2} \right] + \left[k_r \frac{\partial^2 T_{an}}{\partial r^2} \right] \quad (4.90)$$

Table 4.6 Initial and boundary conditions for tube and shell sides (Nalbant Atak et al., 2021)

Conditions	Reaction Side (Tube Side)	Permeation Side (Shell Side)
Initial Conditions	$T_{tube} \big _{t=0} = T_{tube,initial}$	$T_{an} \big _{t=0} = T_{an,initial}$
Boundary Conditions	$T_{tube} \big _{z=0} = T_{feed}$	$T_{an} \big _{z=0} = T_{sweep}$ (Co-current Flow)
		$T_{an} \big _{z=L} = T_{sweep}$ (Counter-current Flow)
	$\frac{\partial T_{tube}}{\partial z} \big _{z=L} = 0$	$\frac{\partial T_{an}}{\partial z} \big _{z=L} = 0$ (Co-current Flow)
		$\frac{\partial T_{an}}{\partial z} \big _{z=0} = 0$ (Counter-current Flow)
	$q \big _{r=r_{i,M}} = -U_M(T_{tube} - T_{an}) + \phi$	$q \big _{r=r_{i,shell}} = -U_{shell}(T_{an} - T_{oven})$
	$\frac{\partial T_{tube}}{\partial r} \big _{r=0} = 0$	$q \big _{r=r_{o,M}} = -U_M(T_{tube} - T_{an}) + \phi$

4.4.2 Model Development

2-D model of a membrane reactor producing hydrogen from methane or biogas was developed using the COMSOL Multiphysics software. Figure 4.6 shows the schematic of 2-D membrane reactor model. In the 2-D model, only the reaction and permeation sides where are found on the two sides of the membrane were investigated. When the feed gas comes to the active catalyst area, the chemical reactions occur and hydrogen production is carried out. The produced hydrogen passes from the reaction side to the permeation side along the active membrane length. The feed gas and sweep gas are fed from the same direction into the membrane reactor.

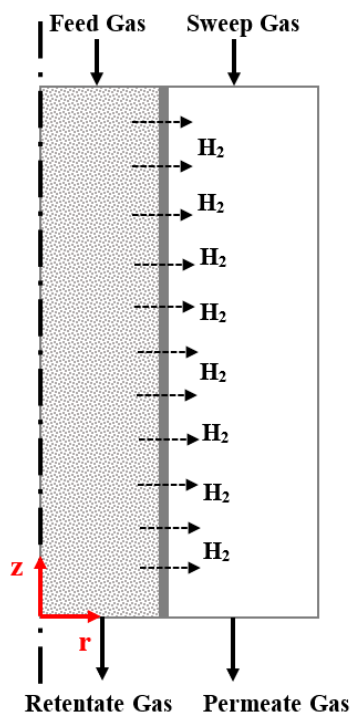


Figure 4.6 Schematic of 2-D membrane reactor model

The 2-D models were created using four different physics such as Transport of Concentrated Species, Chemistry, Darcy's Law, and Heat Transfer in Fluid. In Transport of Concentrated Species physics, changes in the molar fractions of each species are examined according to the reaction sources of chemical reactions taken from Chemistry physics. Also, temperature changes found using Heat Transfer in Fluid physics are important for equations of chemical reactions. Finally, Darcy's Law physics is used to simulate the flow of liquids through porous media. Therefore, the reaction kinetic equations, molar fractions and temperatures are calculated using all these physics together. In this study, methane-steam reforming reactions occur on the reaction side, and as a result, the hydrogen molecules produced pass to the permeation side from the reaction side via the membrane with the Solution-Diffusion mechanism. As a result, the distribution of molar flow rates of species, the distribution of temperatures in the reaction and permeation sides, and the distribution of molar concentration for each species were investigated through the axial and radial directions.

The general equations used in the modeling studies are given below for each physics separately. In Transport of Concentrated Species physics, the variation of the molar fractions of each species according to the reaction sources of chemical reactions has been examined and the used equation is given in Eq. (4.91). The Stefan-Maxwell approach was chosen as the diffusion mechanism.

$$\nabla \cdot j_i + \rho(u \cdot \nabla)\omega_j = R_j \quad (4.91)$$

The terms for the reaction sources of the species (R_j) are taken from "Chemistry" physics. Input molar ratios are chosen as initial conditions. The chemical reactions integrated in Chemistry physics and their reaction kinetic equations are given below (Xu and Froment, 1989).

$$R_1 = k_{0.1} \exp\left(\frac{-E_1}{RT}\right) \left[P_{CH_4} P_{H_2O} - \frac{P_{H_2}^3 P_{CO}}{K_{eq,1}} \right] / (P_{H_2}^{2.5} \cdot DEN^2) \quad (4.92)$$

$$R_2 = k_{0.2} \exp\left(\frac{-E_2}{RT}\right) \left[P_{CO} P_{H_2O} - \frac{P_{H_2} P_{CO_2}}{K_{eq,2}} \right] / (P_{H_2} \cdot DEN^2) \quad (4.93)$$

$$R_3 = k_{0.3} \exp\left(\frac{-E_3}{RT}\right) \left[P_{CH_4} P_{H_2O}^2 - \frac{P_{H_2}^4 P_{CO_2}}{K_{eq,3}} \right] / (P_{H_2}^{3.5} \cdot DEN^2) \quad (4.94)$$

All coefficients used in here are taken from the study of Xu and Froment (1989). In this model, temperature variation is important due to chemical reactions. The molar fraction and temperature are taken into account to calculate the reaction kinetic equations. Heat Transfer in Fluid physics also helps us to find temperature changes through the reactor length. The equation used in this physics is as follows:

$$\rho C_p u \cdot \nabla T_2 + \nabla \cdot q = Q + Q_p + Q_{vd} \quad (4.95)$$

where Q is the heat sources other than viscous diffusion, Q_p is the work done by the pressure changes, and Q_{vd} is the work done by the viscous diffusion.

Finally, Darcy's Law physics examines the pressure changes through the reactor length. Darcy's Law physics is used to simulate the flow of liquids through porous

media. In general, it can be used for modeling low velocity flow or for modeling media with low permeability and porosity. The equations used in this physics are given below.

$$\nabla \cdot (\rho u) = Q_m \quad (4.96)$$

$$u = -\frac{\kappa}{\mu} \nabla p \quad (4.97)$$

where Q_m is the mass source term, κ is the permeability of the porous medium and μ is the dynamic viscosity of the liquid.



CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

In this chapter, the results and discussion of the modeling studies are presented in different subsections. In Section 5.2, the one-dimensional modeling results mentioned in Section 4.2 are given for two different Case Studies. In order to make sure the validation of the developed 1-D models of the membrane reactor, two different case studies were realized. One of these (Case Study-1) is related to the 1-D model study (Alavi et al., 2017) in the literature; the other (Case Study-2) is related to the experimental and modeling study (Iulianelli et al., 2010) in the literature. In Case Study-1, firstly, the first analysis study was done, and the results were compared with the reference study (Alavi et al., 2017) results. However, the error percentages were found as non-acceptable. Then, the solution algorithm was improved by the literature review, and the error percentages were decreased. In Case Study-2, the 1-D model was developed and the results compared with the reference study (Iulianelli et al., 2010) results. To reduce the differences between our model and reference model, the genetic algorithm method was used to identify unknown coefficients by minimizing the difference between the experimental results and the model results. In Section 5.3, the modeling results of an integrated membrane reactor + CO₂ capture system to generate decarbonized hydrogen are presented. The effects of some operating parameters (the operating temperature, the reaction pressure, and the steam-to-carbon ratio) on the system performance (methane conversion, hydrogen yield, CO₂ yield, and thermal efficiency (based on LHV and HHV)) are investigated in detail. In addition, the change of the exergy destructions of all components in the integrated system is investigated according to the different parameters. In Section 5.4, the results of different 2-D models are presented. The changes in the molar flow rates of each species, the distribution of temperatures in the reaction and permeation sides, and the distribution of the molar concentration of species are investigated in the axial and radial directions.

5.2 One-Dimensional Modeling Results

In 1-D modeling study, two different case studies were analyzed and the results were compared with the reference studies. The modeling equations given in Section 4.2 were solved according to the Case Studies and the catalyst location in tube or shell side.

- Within the Case Study-1, the one-dimensional model of a membrane reactor (Figure 5.1-(a)) in which the permeation side is the tube side, while the reaction side is the shell side, was developed. In this study, the change of the molar flow rates of each species and temperatures in the reaction and permeation sides were investigated and then these results were compared with the results of study of Alavi et al. (2017). The performance results along the reactor length (methane conversion and hydrogen recovery) were presented and compared.
- Within the Case study-2, the one-dimensional model of a membrane reactor (Figure 5.1-(b)) in which the permeation side is the shell side, while the reaction side is the tube side was developed. In reference study (Iulianelli et al., 2010), both the experimental and the modeling studies were studied and the results were compared. In this Case Study-2, the results were compared with the reference study (Iulianelli et al., 2010) according to the changing the sweep factor (0.6 and 1.2), reaction pressure (1, 2, and 3 bar), and temperature (400, 450, and 500°C). In addition, the change of temperatures in the reaction and permeation sides were examined.

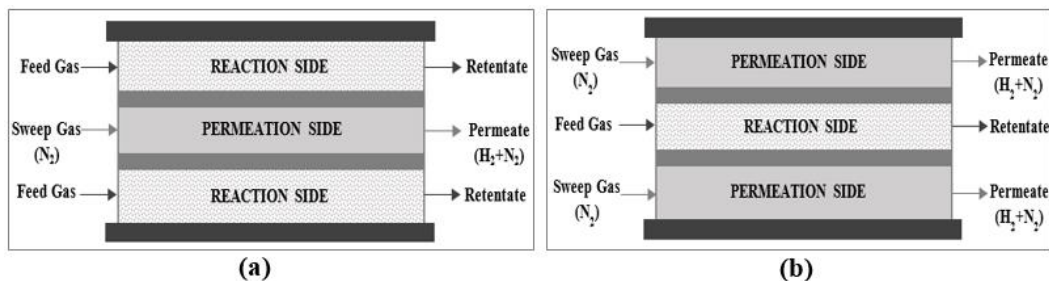


Figure 5.1 Schematics of the membrane reactor used in (a) Case Study-1 and (b) Case Study-2

Figure 5.2 shows the flow chart diagram used in one-dimensional models. As you can see Figure 5.2, firstly, the inlet values (at $z=0$ and $k=0$) used in the reference study are given in the model. These inlet values consist of the molar flow rates of each species in synthetic gas, temperatures and pressures in the reaction and permeation sides, geometric values of the membrane reactor, and the constants used in the reaction kinetics equations. Modeling equations include the reaction kinetics for hydrogen production calculation from synthetic gas, mass and energy balance equations for the reaction and permeation sides, and the equation of hydrogen permeation through membrane. All equations are solved again after each dz distance using the finite difference method. If axial distance, z , is equal to the reactor length, L , the analysis is stopped, and the results are achieved.

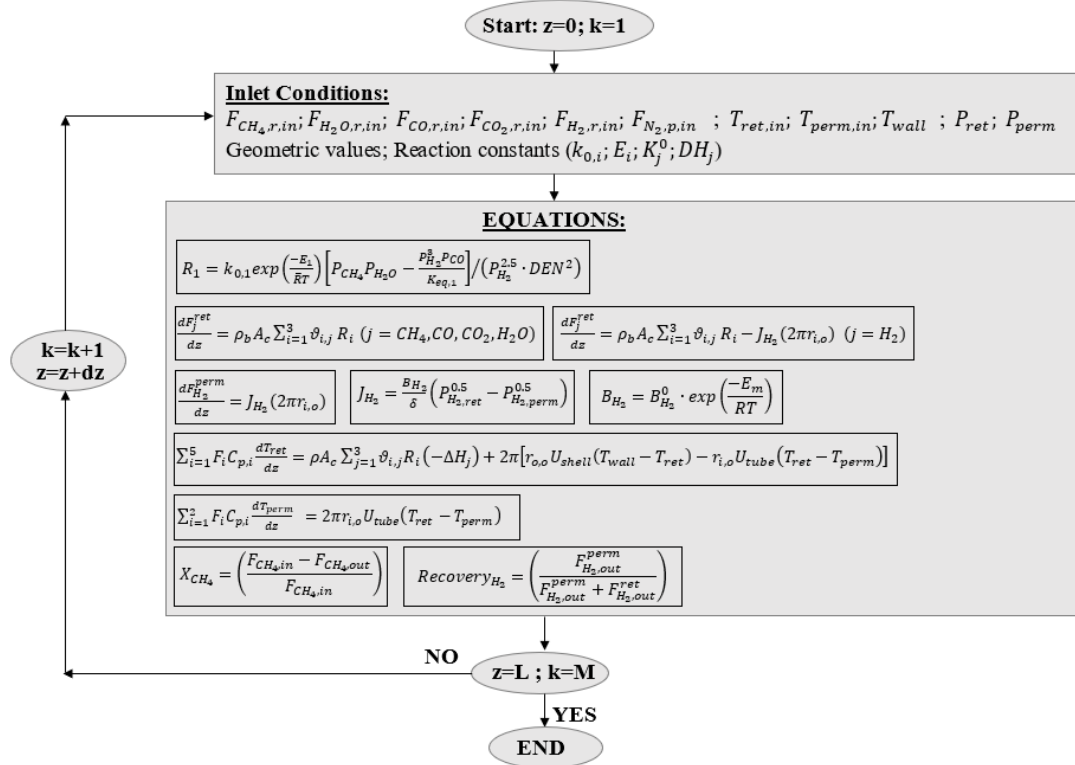


Figure 5.2 Flow chart diagram used in one-dimensional models

5.2.1 Case Study-1

Within the Case Study-1, the one-dimensional model of a membrane reactor consisting of two concentric tubes was developed. In this membrane reactor, the permeation side is the tube side; while the reaction side is the shell side. Firstly, in the

first analysis study, a one-dimensional model was developed and compared with the reference study (Alavi et al., 2017). When the results of the first analysis study were compared, the percent error for the methane conversion, the hydrogen recovery, the retentate temperature, and the permeate temperature was calculated as 73.68%, 13.84%, 12.18%, and 8.43%, respectively. Therefore, the solution algorithm of this 1-D model of membrane reactor used in the Case Study-1 was improved according to our detailed literature review study given in Section 2.7.1. Consequently, the final validation study was done, and the percent error for the methane conversion, the hydrogen recovery, the retentate temperature, and the permeate temperature decreases to 0.26%, 7.69%, 0.24%, and 0.86%, respectively.

In this section, the change of the molar flow rates of each species and temperatures in the reaction and permeation sides were investigated and then these results were compared with the results of Alavi et al. (2017). The performance results along the reactor length (methane conversion and hydrogen recovery) were presented and compared.

5.2.1.1 Assumptions

Table 5.1 shows the used geometric and operating parameters that were taken from the study of Alavi et al. (2017). The assumptions used in this model are given as follows:

- Ideal gas behavior is assumed for each species.
- The flows in reaction and permeation sides are in the same direction (co-current flow).
- Steady-state operation is assumed.
- The pressures for reaction and permeation sides are constant.
- Pre-exponential factor and activation energy used in the calculation of hydrogen flux by Sievert's Law are taken as 7.92×10^{-5} (mol-m/(m²-s-kPa^{0.5})) and 15.7 kJ/mol, respectively (Alavi et al., 2017).

Table 5.1 The operating and design parameters used in this model (Alavi et al., 2017)

Parameter	Value
Reactor length, L	12 m
External tube external radius, $r_{o,o}$	0.0875 m
External tube internal radius, $r_{o,i}$	0.0775 m
Internal tube external radius, $r_{i,o}$	0.045 m
Internal tube internal radius, $r_{i,i}$	0.035 m
Bed density, ρ	1990.6 kg/m ³
Inlet molar flow rate of methane, $F_{CH_4,r,in}$	5 kmol/h
Inlet molar flow rate of sweep gas, $F_{N_2,p,in}$	4x $F_{CH_4,r,in}$
Inlet temperature of the reaction side, $T_{ret,in}$	773 K
Inlet temperature of the permeation side, $T_{perm,in}$	773 K
Inlet pressure of the reaction side, $P_{ret,in}$	29.29 bar
Inlet pressure of the permeation side, $P_{perm,in}$	10.10 bar
Wall temperature, T_{wall}	1200 K

5.2.1.2 The Change of Molar Flow Rates of Species

In the reaction side, the molar flow rates of methane (CH₄) and water (H₂O) decrease, whereas the molar flow rates of carbon dioxide (CO₂) and hydrogen (H₂) increase because of the steam reforming reaction along the reactor length. The change of carbon monoxide (CO) molar flow rate is negligible because of the water-gas shift reaction that consumes CO. In the permeation side, the molar flow rate of H₂ increases through the reactor length due to the passing hydrogen through membrane from the reaction side to the permeation side, while the molar flow rate of N₂ or sweep gas is constant. Figure 5.3 shows the change of molar flow rates for each species in the reaction side through the reactor length for the reference study (Alavi et al., 2017), and this study results. The molar flow rates of CH₄, CO₂, H₂, and H₂O at 12 m for the reference study are 2.57, 2.00, 3.04, and 12.09, respectively. The molar flow rates of CH₄, CO₂, H₂, and H₂O at 12 m for this study are 3.10, 2.09, 2.30, and 12.27, respectively. Table 5.2 shows the variation of molar flow rates of each species for the reference and our studies.

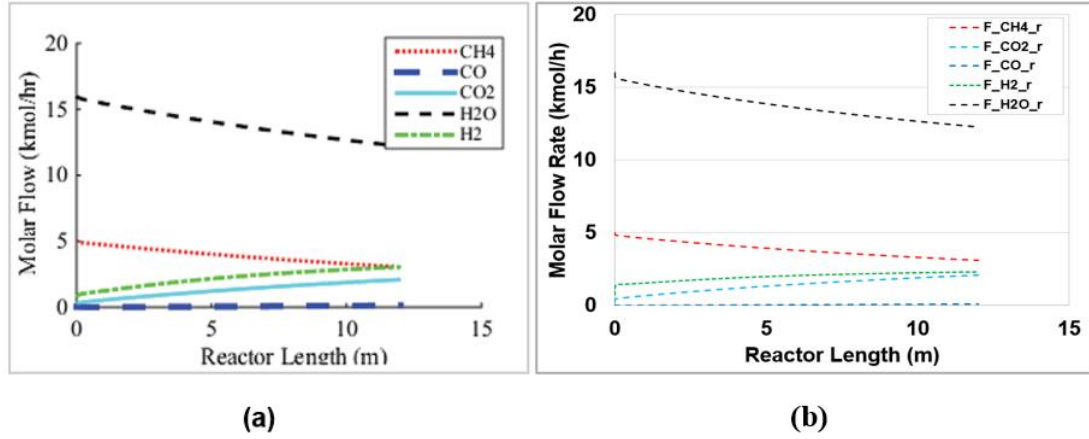


Figure 5.3 The change of molar flow rates for each species in the reaction side; (a) for the reference study and (b) for this study

Table 5.2 The variation of molar flow rates of each species for all studies

Study	Species			
	CH ₄	CO ₂	H ₂	H ₂ O
Ref. Study (Alavi et al., 2017)	2.57	2.00	3.04	12.09
This Study	3.10	2.09	2.30	12.27

5.2.1.3 The Change of Temperature in the Reaction and Permeation Sides

Figure 5.4 shows the comparison about the variation of temperatures in the reaction and the permeation sides along the reactor for the reference study (Alavi et al., 2017), and the this study results.

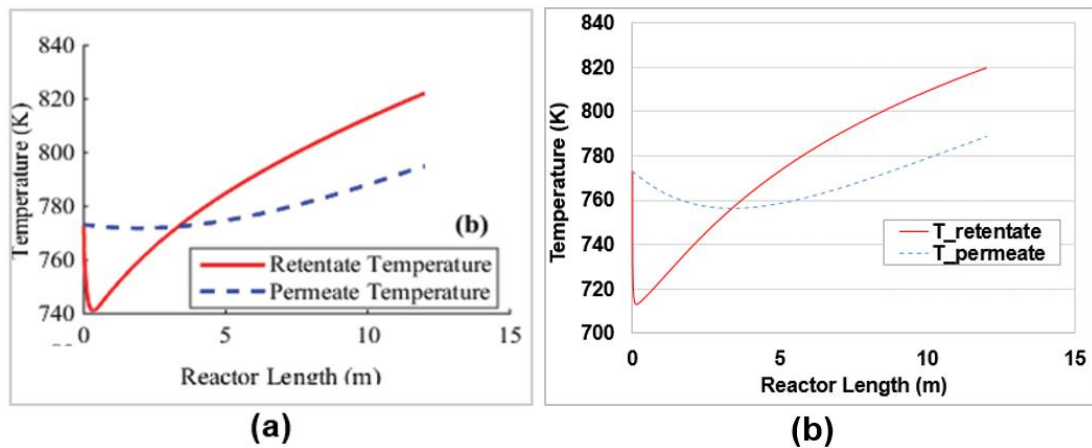


Figure 5.4 The change of temperatures in the reaction and the permeation sides; (a) for the reference study and (b) for this study

In Alavi et al. (2017), the temperature of the reaction side ranges between 773 and 821 K, and the temperature of the permeation side ranges between 773 and 794 K. The results of this study showed that the temperature of the reaction side changes from 773 K to 819 K, while the temperature of the permeation side changes from 773 K to 788 K. Table 5.3 shows the variation of temperatures for the reaction and permeation sides for the reference and our studies. In the final validation study, the error percentages for the reaction and permeation temperatures are found as 0.24% and 0.86%, respectively.

Table 5.3 The variation of molar flow rates of each species for all studies

Study	Outlet Temperatures	
	$T_{retentate}$	$T_{permeate}$
Ref. Study (Alavi et al., 2017)	821 K	794 K
Our Study	819 K	788 K

5.2.1.4 The Change of Methane Conversion

Figure 5.5 shows the simulations about the methane conversion variation along the reactor, including also the simulations of Alavi et al. (2017).

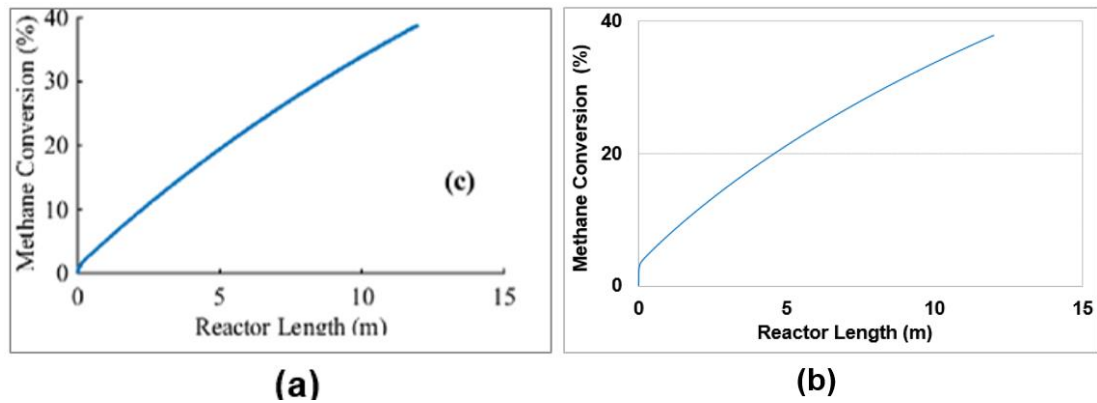


Figure 5.5 The change of methane conversion; (a) for the reference study and (b) for our study

As you can see from Figure 5.5, the results of our study is found as very close to the reference study. Methane conversion for this study and the reference study were found as 38.1% and 38%, respectively. After the solution algorithm of this 1-D model of membrane reactor used in the Case Study-1 was improved, the error percentage between one-dimensional model and the reference study was decreased from 73.68%

to 0.26 %. Similar to Figure 5.5, Figure 5.6 shows the hydrogen recovery trends, which in the reference study and this study results.

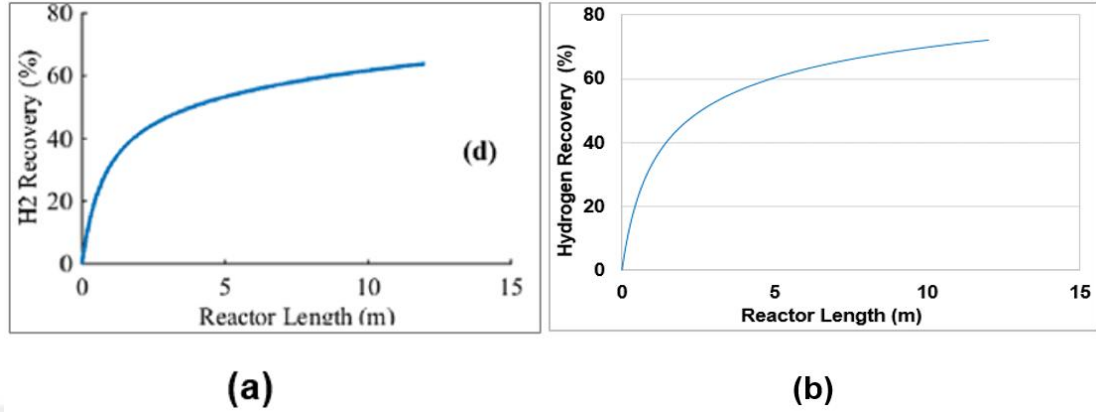


Figure 5.6 The change of membrane reactor performance through reactor length for (a) for the reference study and (b) for our study

As can be seen from Figure 5.6, the results of the final validation study is close with the reference study. Hydrogen recovery values for the reference study and this study are found as 65% and 70%, respectively. After the solution algorithm of this 1-D model of membrane reactor used in the Case Study-1 was improved, the error percentage between one-dimensional model and the reference study was decreased from 13.84% to 7.69%.

5.2.2 Case Study-2

Within the Case Study-2, the one-dimensional model of a membrane reactor consisting of two concentric tubes was developed. In this membrane reactor, the permeation side is the shell side; while the reaction side is the tube side as shown in Figure 5.1-(b). The 1-D model was developed using the experimental data (Iulianelli et al., 2010) that are given for the self-standing membrane. In reference study (Iulianelli et al., 2010), both the experimental and the modeling studies were studied and the results were compared. In Case Study-2, the results between the reference and our modeling study were compared with the changing the sweep factor (0.6, 1.2, and 1.6), reaction pressure (1, 2, and 3 bar), and temperature (400, 450, and 500°C). In addition, the change of temperatures in the reaction and permeation sides at 1.2 sweep

factor, 450°C, and 2 bar. Within the scope of Case Study-2, the genetic algorithm method for 400°C and 1.2 sweep factor conditions was used to identify unknown coefficients by minimizing the difference between the experimental results and the model results in the 1-D model.

5.2.2.1 Assumptions

The assumptions used in this model are given as follows:

- Ideal gas behavior is assumed for each species.
- The flows in reaction and permeation sides are in the same direction (co-current flow).
- Steady-state operation is assumed.
- The pressures for reaction and permeation sides are constant.
- Pre-exponential factor and activation energy used in the calculation of hydrogen flux by Sievert's Law are taken as 1.4×10^{-6} (mol-m/(m²-s-kPa^{0.5})) and 8.7 kJ/mol, respectively (Iulianelli et al., 2010).

Table 5.4 shows the used geometric and operating parameters that were taken from the study of Iulianelli et al. (2010).

Table 5.4 The operating and design parameters used in this model (Iulianelli et al., 2010)

GEOMETRIC PARAMETERS	
Parameter	Value (Unit)
Membrane length	145 mm
Membrane thickness	50 μ m
Inner diameter of membrane	9.9 mm
Outer diameter of membrane	10 mm
Outer tube outer diameter, $d_{o,o}$	28 mm
Outer tube inner diameter, $d_{o,i}$	20 mm
Inner tube outer diameter, $d_{i,o}$ (it corresponds to the membrane outer diameter)	10 mm
Inner tube inner diameter, $d_{i,i}$ (it corresponds to the membrane inner diameter)	9.9 mm
OPERATING PARAMETERS	
Parameter	Value (Unit)
Catalyst mass	3 g
Inlet temperature of the reaction side	450 °C
Inlet temperature of the permeation side	450 °C
Inlet pressure of the reaction side	1-5 bar
Inlet pressure of the permeation side	1 bar
Steam-to-carbon ratio (H_2O/CH_4)	2/1
Sweep factor (N_2/CH_4)	1.6
Inlet molar flow rate of CH_4 in reaction side	0.17 mol/h
Inlet molar flow rate of N_2 in reaction side (standard gas)	0.05 mol/h
Inlet molar flow rate of N_2 in permeate side (standard gas)	0.27 mol/h
Type of membrane	Tubular, self-supported Pd-Ag
Type of catalyst	Commercial (Catal. Intern. Ltd)
Catalyst location (Shell or tube)	Tube
Flow type (parallel or counter)	Parallel (co-current)
Method of heating of reactor	Electric
Wall temperature of the reactor or heat flux to the reactor	450 °C

5.2.2.2 First Analysis Results for Case Study-2

In the reference study, Iulianelli et al. (2010) studied both experimental and isothermal modeling of the membrane reactor with Pd-based self-supported membrane. In Case Study-2, the results of our study were compared with the experimental and modeling results of the reference study for different conditions. Table 5.5 shows the effect of the reaction pressure on the methane conversion and hydrogen recovery at 400°C and 0.12 sweep factor for our study and reference study (experimental and modeling). As you can see, the methane conversion results of our model and the reference model decreases with increasing pressure, however, the methane conversion results of our model is different from the experimental results. When the reaction pressure changes from 1 to 3 bars, the error of hydrogen recovery

between our model and the experimental studies was calculated as 11.76%, 24.3%, and 24.78%, respectively.

Table 5.5 The comparison of the methane conversion and hydrogen recovery at 400°C and 0.12 SF

Performance	Pressure, bar	Our Model	Experimental (Iulianelli et al., 2010)	Model (Iulianelli et al., 2010)
Conversion (%)	1	19.68	10.09	10.83
	2	17.18	10.34	9.35
	3	15.94	13.30	8.86
Recovery (%)	1	3.90	3.44	4.40
	2	9.09	6.88	9.05
	3	15.33	11.53	13.70

Table 5.6 shows the effect of the reaction pressure on the methane conversion and hydrogen recovery at 400°C and 1.2 sweep factor for our and reference studies (experimental and modeling). The hydrogen recovery results of our study and the reference study are found as very similar. When the reaction pressure changes from 1 to 3 bars, the error of hydrogen recovery between our model and the experimental studies was calculated as 0.18%, 1.77%, and 2.03%, respectively. However, the methane conversion results of our model is different from the experimental results.

Table 5.6 The comparison of the methane conversion and hydrogen recovery at 400°C and 1.2 SF

Performance	Pressure, bar	Our Model	Experimental (Iulianelli et al., 2010)	Model (Iulianelli et al., 2010)
Conversion (%)	1	21.80	13.01	13.50
	2	21.14	17.97	13.81
	3	21.29	23.16	15.09
Recovery (%)	1	26.62	26.57	30.69
	2	44.49	43.70	49.27
	3	56.16	55.02	61.56

➤ *The Effect of Sweep Factor on Methane Conversion and Hydrogen Recovery*

Table 5.7 shows the effect of the sweep factor with the changing pressure on the methane conversion and hydrogen recovery at 450°C for our model and reference result. When the sweep factor increases from 0.6 to 1.6, the difference of modeling and experimental results increases. This reason can be related to the constants used in the hydrogen flux equation. These constants were taken from the experimental study (Iulianelli et al., 2010). However, these data were obtained by the pure hydrogen

permeation flux experiments at the different temperatures. In real applications, this flux is different, if the hydrogen is mixed with the other gases, since some effects such as concentration polarization, dilution etc. which decrease the hydrogen permeation flux can negatively affect the hydrogen permeation performance. This is responsible for the change of the driving force of the hydrogen permeation and could give the mismatch between our model and experimental results.

Table 5.7 The comparison of the methane conversion and hydrogen recovery at 450°C with the changing sweep factor and pressure

Performance	SF	Pressure, bar	Our Model	Experimental (Iulianelli et al., 2010)
Conversion (%)	0.6	1	21.48	22.89
		2	19.85	26.23
		3	19.50	27.84
	1.2	1	22.59	22.58
		2	21.72	27.099
		3	21.84	31.36
	1.6	1	23.18	43.93
		2	22.63	48.51
		3	22.94	50.12
Recovery (%)	0.6	1	16.36	19.64
		2	31.25	24.93
		3	43.10	43.57
	1.2	1	26.96	26.18
		2	45.00	43.64
		3	56.73	56.60
	1.6	1	32.16	36.77
		2	50.74	61.21
		3	61.94	70.27

➤ *The Effect of Temperature on Methane Conversion and Hydrogen Recovery*

In the membrane reactor, the inlet temperatures of feed gas and sweep gas are the same. The steam-methane reforming reactions occur and the hydrogen is produced in the reaction side and some of this produced hydrogen pass through the membrane to the permeation side. Table 5.8 shows the effect of the temperature with the changing pressure on the methane conversion and hydrogen recovery at 1.2 sweep factor for our model and experimental results.

Table 5.8 The comparison of the methane conversion and hydrogen recovery at 1.2 SF with the changing temperature and pressure

Performance	Temperature, °C	Pressure, bar	Our Model	Experimental (Iulianelli et al., 2010)
Conversion (%)	400	1	21.80	13.01
		2	21.14	17.97
		3	21.29	23.16
	450	1	22.59	22.58
		2	21.72	27.099
		3	21.84	31.36
	500	1	24.43	29.96
		2	22.79	32.44
		3	22.72	34.66
Recovery (%)	400	1	26.62	26.57
		2	44.49	43.70
		3	56.16	55.02
	450	1	26.96	26.18
		2	45.00	43.64
		3	56.73	56.60
	500	1	27.78	29.67
		2	45.98	53.61
		3	57.62	62.84

Temperature affects the reaction rates of the reforming reactions. When the temperature increases, the reaction kinetics increase. If the temperature is higher than 450°C, the self-supported Pd-based membrane begins to be damaged and can not function over time. As you can see, the methane conversion and hydrogen recovery of our model are matched well with the experimental result at 450°C. When the reaction pressure changes from 1 to 3 bars, the error of methane conversion between our model and the experimental studies at 450°C was calculated as 0.044%, 24.76%, and 43.58%, respectively. When the reaction pressure changes from 1 to 3 bars, the error of hydrogen recovery between our model and the experimental studies at 450°C was calculated as 3.59%, 3.13%, and 0.088%, respectively. Figure 5.7 shows the comparison of methane conversion and hydrogen recovery between our model and experimental results for 450°C, 1.2 SF, and 2 SC.

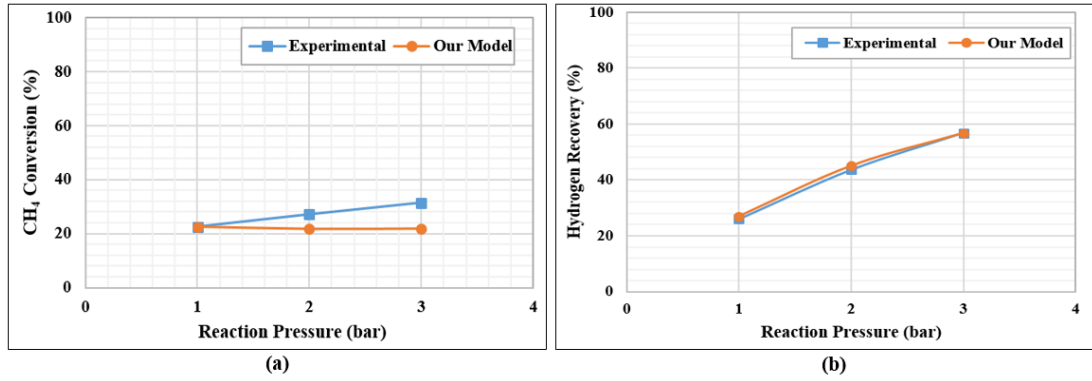


Figure 5.7 The comparison of methane conversion and hydrogen recovery between our model and experimental results for 450°C, 1.2 SF, and 2 SC

Figure 5.8 shows the changes of temperature in the reaction and the permeation sides through the reactor length at 450°C, 1.2 SF, and 2 SC. The wall temperature is constant and equals to 450°C (723 K). The shell and tube sides are the permeation and the reaction sides, respectively. Therefore, the temperature in the permeation side is higher than the temperature of the reaction side. The trend of temperature change in the reaction side is similar to the temperature change in Case Study-1. The reason of this situation can be related to the steam-methane reforming reactions.

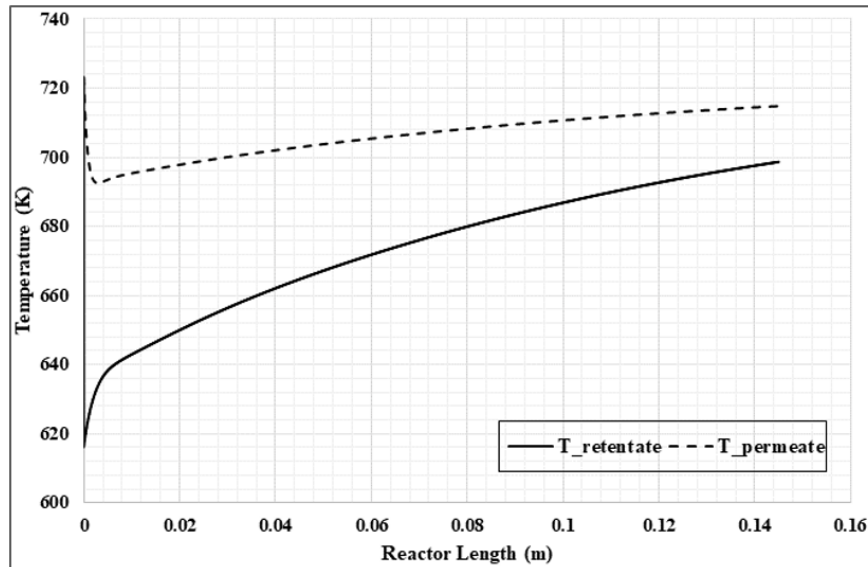


Figure 5.8 The changes of temperature in the reaction and the permeation sides through the reactor length at 450°C, 1.2 SF, and 2 SC

5.2.2.3 Genetic Algorithm Results

Genetic algorithm is the optimization method based on a natural selection process for both constrained and unconstrained problems. The genetic algorithm method is suitable to solve different problems in which the objective function is nonlinear, discontinuous, and non-differentiable. The reason for the using genetic algorithm method is that the coefficients in the reaction kinetic equations for the reference study are not known. These coefficients are a total of six variables, including the exponential factors ($k_{0,1}$, $k_{0,2}$, and $k_{0,3}$) and the activation energies (E_1 , E_2 , and E_3) of each chemical reaction. Firstly, the lower, upper, and initial guess values of these coefficients are entered into the model code. After an objective function has been determined in a one-dimensional mathematical code, the goal is to make the objective function minimal. Figure 5.9 shows the genetic algorithm code including the lower, upper, and initial guess values, six variables, and the objective function and the result.

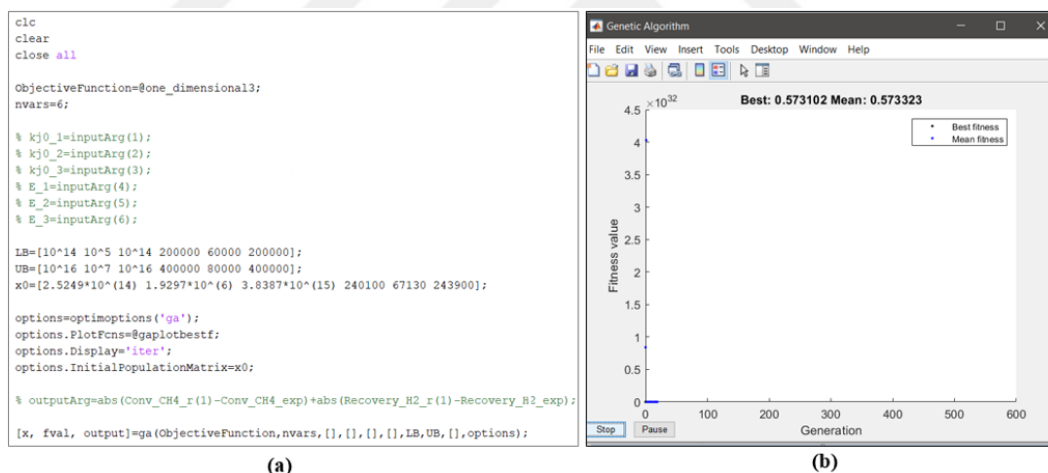


Figure 5.9 Genetic algorithm method used in MATLAB; (a) Code and (b) Result

The closer the best value and the mean value given in Figure 5.9-(b) are to each other, the more minimal the objective function in the genetic algorithm method will be so close to the target (minimum). As you can see Figure 5.9-(b), the best and the mean values are equal and this value is 0.573. Finally, after these values are equal, MATLAB code is stopped and the results of the calibrated variables are obtained (Table 5.9).

Table 5.9 Lower, upper, initial guess, and calculated values of calibrated variables

	$k_{0,1}$	$k_{0,2}$	$k_{0,3}$	E_1	E_2	E_3
Lower	10^{14}	10^5	10^{14}	200,000	60,000	200,000
Upper	10^{16}	10^7	10^{16}	400,000	80,000	400,000
Initial Guess	$2.5249 \cdot 10^{14}$	$1.9297 \cdot 10^6$	$3.8387 \cdot 10^{15}$	240,100	67,130	243,900
Calculated Value	$8.545 \cdot 10^{15}$	$6.8234 \cdot 10^5$	$7.7246 \cdot 10^{15}$	260,260	78,274	354,500

When calculated values in Table 5.9 were used in the 1-D model, our model results and the experimental results in the reference study (Iulianelli et al., 2010) were compared according to the methane conversion and the hydrogen recovery. Table 5.10 shows the comparison between our model and experimental results at 400°C and 1.2 sweep factor after the genetic algorithm method.

Table 5.10 Comparison between our model and experimental results at 400°C and 1.2 sweep factor after the genetic algorithm method

	Our Model	Experimental (Iulianelli et al., 2010)	Error
Methane Conversion	17.63%	17.97%	1.92%
Hydrogen Recovery	44.20%	43.70%	1.14%

As can be seen from the comparison after the genetic algorithm method in Table 6.11, the error percentages for methane conversion and hydrogen recovery are calculated as 1.92% and 1.14%, respectively. Thus, the methane conversion and the hydrogen recovery values at 400°C and 1.2 SF depending on the changing reaction pressure (1, 2, and 3 bar) were investigated by using the calculated variables from the genetic algorithm method. Table 5.11 shows the effect of the reaction pressure on the methane conversion and hydrogen recovery at 400°C and 1.2 sweep factor for our model and reference experimental study.

Table 5.11 Comparison of the methane conversion and hydrogen recovery at 400°C and 1.2 SF

Performance	Pressure, bar	Our Model	Experimental (Iulianelli et al., 2010)	Error
Conversion (%)	1	30.39	13.01	57.19%
	2	17.63	17.97	1.92%
	3	30.35	23.16	23.69%
Recovery (%)	1	27.23	26.57	2.42%
	2	44.20	43.70	1.14%
	3	58.53	55.02	5.99%

The hydrogen recovery results of our model and the reference experimental study are found as very similar. When the reaction pressure changes from 1 to 3 bars, the error of hydrogen recovery between our model and the experimental studies was calculated as 2.42%, 1.14%, and 5.99%, respectively, and this error percentage is relatively acceptable. This error of methane conversion between our model and the experimental studies was calculated as 57.19%, 1.92%, and 23.69%, respectively, and this error percentage cannot acceptable due to the high difference between our model and experimental. Therefore, in this thesis report, the effects of sweep factor and temperature with the changing reaction pressure on only hydrogen recovery are investigated and discussed.

5.2.2.4 The Effect of Sweep Factor on Hydrogen Recovery

After the genetic algorithm method, the effect of the sweep factor with the changing pressure on the hydrogen recovery at 450°C for this model is shown in Figure 5.10. When the sweep factor value is taken as 0.6, the hydrogen recovery at 1, 2, and 3 bar are calculated as 15.49%, 27.76%, and 37.38%, respectively. Furthermore, when the sweep factor value is taken as 1.2, the hydrogen recovery at 1, 2, and 3 bar are calculated as 26.85%, 44.37%, and 55.8%, respectively.

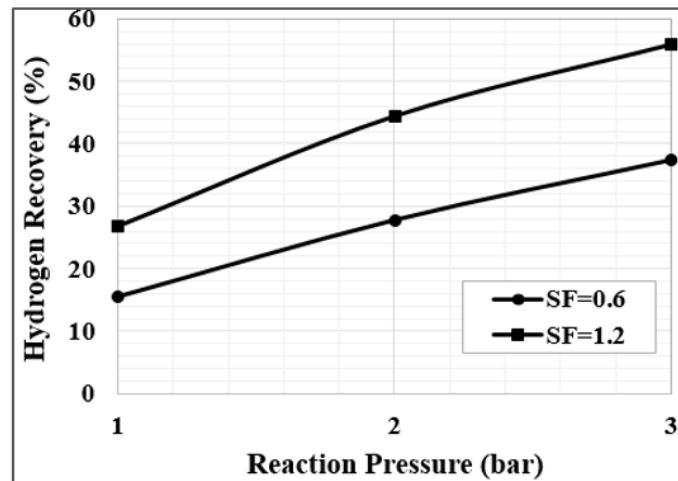


Figure 5.10 The effect of sweep factor on hydrogen recovery at 450°C with the changing reaction pressure

When the calibration conditions are changed and the results of our model and the experimental are compared, the differences are observed again. This reason can be related to the constants used in the hydrogen flux equation. These constants were taken from the experimental study (Iulianelli et al., 2010). However, these data were obtained by the pure hydrogen permeation flux experiments at the different temperatures. In real applications, this flux is different, if the hydrogen is mixed with the other gases, since some effects such as concentration polarization, dilution etc. which decrease the hydrogen permeation flux can negatively affect the hydrogen permeation performance. This is responsible for the change of the driving force of the hydrogen permeation and could give the mismatch between our model and experimental results.

5.2.2.5 The Effect of Temperature on Hydrogen Recovery

In the membrane reactor, the inlet temperatures of feed gas and sweep gas are assumed as the same. The steam-methane reforming reactions occur and the hydrogen is produced in the reaction side and some of this produced hydrogen pass through the membrane to the permeation side. Figure 5.11 shows the effect of the temperature with the changing pressure on the hydrogen recovery at 1.2 sweep factor. As you can see in Figure 5.11, the hydrogen recovery increases as a function of temperature and pressure. The reasons are that the higher hydrogen permeating flux occurs with the increasing temperature as well as hydrogen permeation driving force increases with the increasing difference between reaction and permeation pressures. These two reasons provide a higher hydrogen recovery in the membrane reactor. Moreover, temperature affects the reaction rates of the reforming reactions. When the temperature increases, the reaction kinetics increase.

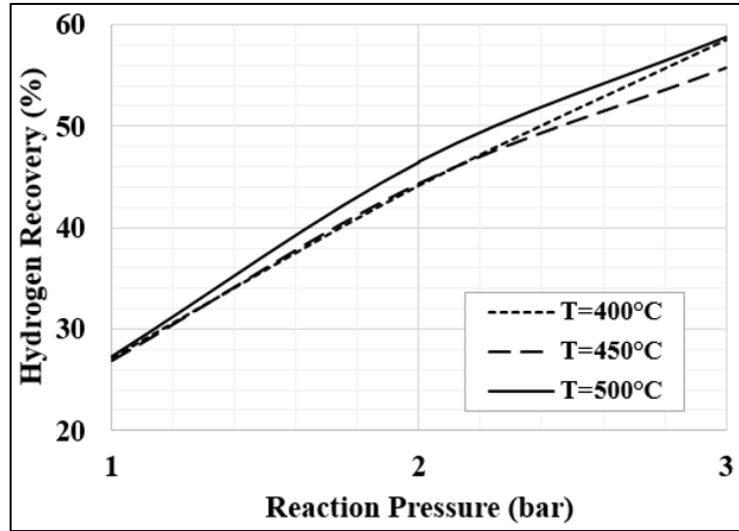


Figure 5.11 Effect of the temperature with the changing pressure on the hydrogen recovery at 1.2 SF

The hydrogen recovery values at 2 bar for 400°C, 450°C, and 500°C are calculated as 44.20%, 44.37%, and 46.47%, respectively; whereas, the hydrogen recovery values 450°C for 1, 2, and 3 bar are calculated as 26.85%, 44.37%, and 55.81%, respectively. The error percentage between our model and the experimental study for 1, 2, and 3 bar at 400°C is calculated as 2.42%, 1.13%, and 5.98%, respectively; whereas, the error for 1, 2, and 3 bar at 450°C is calculated as 2.49%, 1.64%, and 1.41%, respectively. Hydrogen recovery values for 400°C and 450°C are acceptable matched with the experimental study. However, the error value for 1, 2, and 3 bar at 500°C is calculated as 8.56%, 15.36%, and 6.83%, respectively. The error values for 500°C should not acceptable.

5.3 Results of an Integrated System Level Model Including Membrane Reactor and CO₂ Capture System to Generate Decarbonized Hydrogen

In the integrated system-level model, the energy and exergy analyses are conducted with the assumption of 128 reactor tubes, after the validation of membrane reactor model. Table 5.12 gives the values of molar flow rate, temperature, enthalpy, entropy, and total exergy for each point in the integrated system for the baseline simulation.

Table 5.12 Molar flow rate, temperature, enthalpy, entropy, and total exergy for each point for the baseline simulation

State No.	Species	Molar Flow Rate (mol/s)	Temperature (K)	Pressure (bar)	Enthalpy (J/mol)	Entropy (J/mol-K)	Exergy (J/mol)
1	Water	17.06	400.00	3	9602	28.85	1087
2	Water	17.06	400.07	9	9615	28.86	1098.9
3	Water	17.06	888.84	9	67274	146.28	23763
4	Methane	13.33	400.00	1	18475	118.34	553.85
5	Methane	4.00	400.00	1	18475	118.34	832200
6	Methane	5.33	400.00	1	18475	118.34	553.85
7	Methane	4.00	400.00	1	18475	118.34	832200
8	Methane	5.33	618.91	9	28762	120.37	10235
9	Methane and Water	23.52	773.00	9	55339	138.25	221660
10	Retentate Gas	22.38	681.16	1	50239	150.93	197400
11	Dry Air (O ₂ +N ₂)	285.72	865.95	1	26005	226.69	7726.3
12	Dry Air (O ₂ +N ₂)	85.72	865.95	1	26005	226.69	7855.4
13	Dry Air (O ₂ +N ₂)	200.00	865.95	1	26005	226.69	7855.4
14	Hot Flue Gas	170.00	950	1	31029	222.46	10911
15	Exhaust Gas-2	170.00	934.83	1	30524	221.93	10566
16	Exhaust Gas-1	79.71	1160.00	1	41234	224.88	17328
17	Mixture of Exhaust Gases	272.09	974.83	1	35283	217.34	11576
18	Carbon Dioxide	9.19	974.83	1	54342	174.78	15920
19	Other Gases	262.90	974.83	1	34617	218.83	27390
20	Cooling Water	4.77	298	1	1877.3	6.57	1.49
21	Cooling Water	4.77	363	1	48067	151.26	3072
22	Hydrogen	2.89	744.87	1	21000	134.47	241200
23	Other Gases	262.90	423	1	16912	192.28	17597

Exergy destruction related ratios for three main components and the other components as defined in Eq. (4.77) are shown in Figure 5.12. Figure 5.12 shows that the exergy destruction rate of the burner are the highest with 49%, which is followed by the boiler with 36%, and then by the MR with 14%. Non-isothermal mixing in these components and the reaction kinetics in the steam-methane reforming reactions are the main reasons for the high value of the exergy destructions in these components.

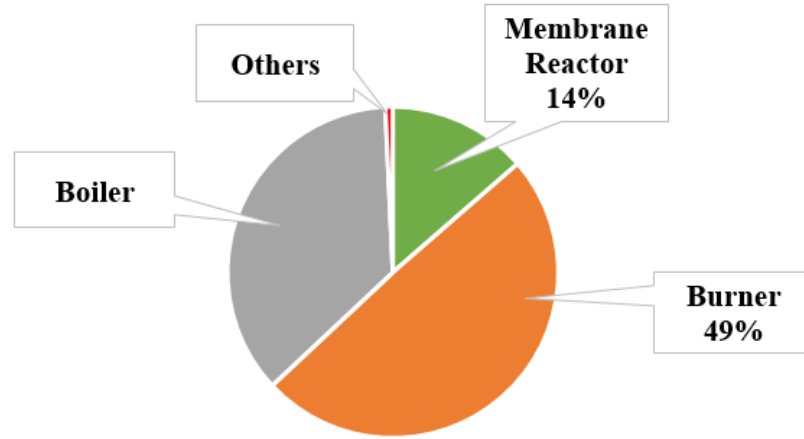


Figure 5.12 The ratio of y_D for the baseline simulation

5.3.1 The Effect of Operating Temperature of the MR

Operating temperature is a critical parameter that affects directly the performance of MR, since the rates of the reaction kinetics equations and the permeating hydrogen flux equation used in the membrane reactor strongly depend on the operating temperature of the MR. In general, when the operating temperature increases, the reaction rates and the hydrogen permeating flux through membrane increase. However, the operating temperature should be defined with considering the thermal durability of the membrane. Figure 5.13 shows the change of system performance assessment values with the operating temperature of membrane reactor.

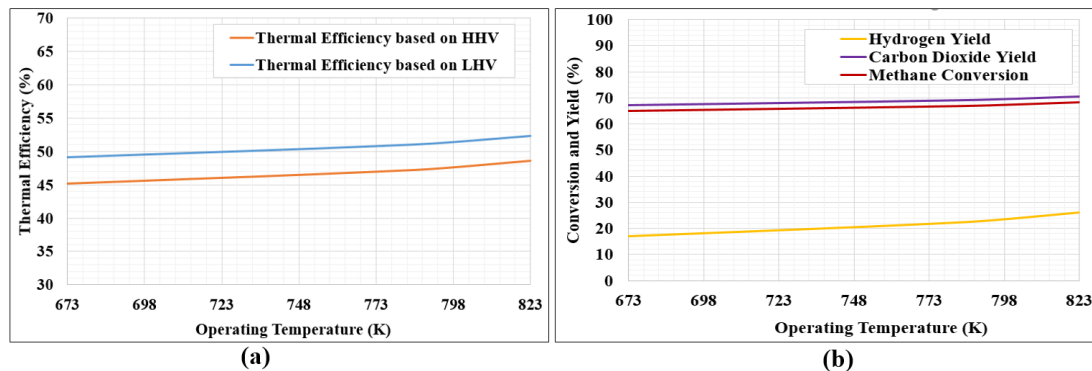


Figure 5.13 The change for (a) thermal efficiency based on HHV and thermal efficiency based on LHV and (b) methane conversion, hydrogen yield, and CO₂ yield with the operating temperature of MR

As can be seen from Fig. 6-(a), when the reaction pressure in the MR increases from 5 bar to 15 bar, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the system increase by 4.1% and 3.7%, respectively. The reason for the increase in the thermal efficiencies can be explained that when the reaction pressure increases from 5 bar to 15 bar, the molar flow rate of hydrogen production from methane increases by 44.8%, and the rate of useful heat almost keeps constant. As can be seen from Fig. 6-(b), when the reaction pressure in the MR increases from 5 bar to 15 bar, the molar flow rate of hydrogen in the permeate stream increases from 2.3 mol/s to 3.3 mol/s. In addition, the molar flow rate of CO₂ in the retentate stream and the depletion of methane in the system almost keep constant. Consequently, when the reaction pressure increases from 5 bar to 15 bar, the increase in the hydrogen yield can be calculated as 44.84%; whereas the CO₂ yield and methane conversion are constant. In addition to the performance results, Table 9 shows the effects of the inlet pressure on reaction side of MR on the exergy destruction rate of each component in the integrated system.

Table 5.13 The values of exergy destruction rate (W) of each component according to the operating temperature of MR

T (K)	Pump	Comp.	Mixer-1	Mixer-2	Burner
673	20	3.23x10 ³	5x10 ³	2.85 x10 ⁴	3.04x10 ⁶
693	20	3.23x10 ³	5.81x10 ³	2.90 x10 ⁴	3.04x10 ⁶
713	20	3.23x10 ³	6.69x10 ³	2.95 x10 ⁴	3.04x10 ⁶
733	20	3.23x10 ³	7.62x10 ³	3.01 x10 ⁴	3.04x10 ⁶
753	20	3.23x10 ³	8.59x10 ³	3.074 x10 ⁴	3.04x10 ⁶
773	20	3.23x10 ³	9.62x10 ³	3.14 x10 ⁴	3.04x10 ⁶
793	20	3.23x10 ³	1.07x10 ⁴	3.19 x10 ⁴	3.04x10 ⁶
823	20	3.23x10 ³	1.23x10 ⁴	3.22 x10 ⁴	3.04x10 ⁶
T (K)	Boiler	MR	CO₂ capture system	Air Valve	CH₄ Valve
673	2.37x10 ⁶	6.08x10 ⁵	651.28	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
693	2.34x10 ⁶	6.53x10 ⁵	654.25	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
713	2.31x10 ⁶	6.98x10 ⁵	657.26	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
733	2.29x10 ⁶	7.44x10 ⁵	660.31	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
753	2.26x10 ⁶	7.91x10 ⁵	663.44	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
773	2.23x10 ⁶	8.39x10 ⁵	666.84	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
793	2.20x10 ⁶	8.94x10 ⁵	670.97	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
823	2.16x10 ⁶	1.01x10 ⁶	681.56	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³

As can be seen from Table 5.13, when the operating temperature of MR increases from 673 K to 823 K, the exergy destruction rates of water pump, compressor, burner, air valve, and methane valve do not change, however, the exergy destruction rates of

MR, Mixer-1, Mixer-2, and CO₂ capture system increase by 66.11%, 146%, 13%, and 4.6%, respectively; and that of the boiler decreases by 8.8%. Consequently, increasing the operating temperature of membrane reactor increases the system performance. However, the rates of degradation of MR, Mixer-1, Mixer-2, and CO₂ capture system increase; and thus, its long-term stability of the integrated system is affected negatively.

5.3.2 The Effect of Reaction Pressure on the MR

In the integrated system model, the pressure values of all state numbers are defined according to the operating conditions of the MR. The inlet pressure of feed gas in the membrane reactor is an important parameter affecting the hydrogen driving force from the reaction side to the permeation side besides the calculations of the reaction rates. Figure 5.14 shows the change of system performance assessment values with the inlet pressure on reaction side of MR.

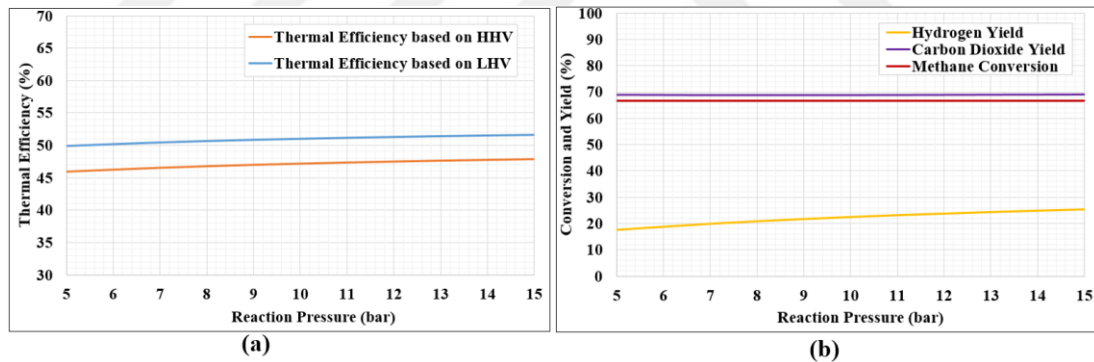


Figure 5.14 The change for (a) thermal efficiency based on HHV and thermal efficiency based on LHV and (b) methane conversion, hydrogen yield, and CO₂ yield with the reaction pressure of MR

As can be seen from Figure 5.14-(a), when the reaction pressure in the MR increases from 5 bar to 15 bar, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the system increase by 4.1% and 3.7%, respectively. The reason for the increase in the thermal efficiencies can be explained that when the reaction pressure increases from 5 bar to 15 bar, the molar flow rate of hydrogen production from methane increases by 44.8%, and the rate of useful heat almost keeps constant. As can be seen from Figure 5.14-(b), when the reaction pressure in the MR increases

from 5 bar to 15 bar, the molar flow rate of hydrogen in the permeate stream increases from 2.3 mol/s to 3.3 mol/s. In addition, the molar flow rate of CO₂ in the retentate stream and the depletion of methane in the system almost keep constant. Consequently, when the reaction pressure increases from 5 bar to 15 bar, the increase in the hydrogen yield can be calculated as 44.84%; whereas the CO₂ yield and methane conversion are constant. In addition to the performance results, Table 5.14 shows the effects of the inlet pressure on reaction side of MR on the exergy destruction rate of each component in the integrated system. As can be seen from Table 5.14, when the inlet pressure of feed gas in MR increases from 5 bar to 15 bar, the exergy destruction rates of burner, boiler, air valve, and methane valve do not change and the exergy destruction rate of CO₂ capture system almost keeps constant, however, the exergy destruction rates of MR, water pump, and compressor increase by 45.8%, 500%, and 55.5%, respectively; and that of the Mixer-1 and Mixer-2 decrease by 56% and 3.7%, respectively. Consequently, increasing the reaction pressure in MR increases the system performance. However, the rates of degradation of main component that is MR increases; and thus, its long-term stability of the integrated system is affected negatively.

Table 5.14 The values of exergy destruction rate (W) of each component according to the inlet pressure on reaction side of MR

P (bar)	Pump	Comp.	Mixer-1	Mixer-2	Burner
5	6.66	2.47x10 ³	1.42x10 ⁴	3.22x10 ⁴	3.04x10 ⁶
7	12.33	2.91x10 ³	1.15x10 ⁴	3.16x10 ⁴	3.04x10 ⁶
9	20	3.23x10 ³	9.62x10 ³	3.14 x10 ⁴	3.04x10 ⁶
11	26.68	3.47x10 ³	8.21x10 ³	3.12 x10 ⁴	3.04x10 ⁶
13	33.36	3.67x10 ³	7.12x10 ³	3.10 x10 ⁴	3.04x10 ⁶
15	40.05	3.84x10 ³	6.23x10 ³	3.10 x10 ⁴	3.04x10 ⁶
P (bar)	Boiler	MR	CO₂ capture system	Air Valve	CH₄ Valve
5	2.23x10 ⁶	6.75x10 ⁵	667.48	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
7	2.23x10 ⁶	7.67x10 ⁵	666.96	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
9	2.23x10 ⁶	8.39x10 ⁵	666.84	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
11	2.23x10 ⁶	8.96x10 ⁵	666.86	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
13	2.23x10 ⁶	9.44x10 ⁵	666.94	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³
15	2.23x10 ⁶	9.84x10 ⁵	667.03	4.65x10 ⁻¹⁰	4.54x10 ⁻¹³

5.3.3 The Effect of S/C in the MR

The molar flow rates of water and methane entering the membrane reactor, are calculated according to the given steam-to-carbon ratio value. The S/C value is defined as follows:

$$S/C = \frac{\dot{n}_{9,H_2O}}{\dot{n}_{9,CH_4}} = \frac{\dot{n}_1}{\dot{n}_6} \quad (5.1)$$

Figure 5.15 shows the change of system performance assessment values with the steam-to-carbon ratio. As can be seen from Figure 5.15-(a), when the S/C increases from 2 to 4, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the overall system increase by 13.6% and 13.7%, respectively. This trend occurs because when the S/C increases, the molar flow rate of the water entering the membrane reactor increases from 10.7 mol/s to 21.3 mol/s. The produced hydrogen from the membrane reactor increases by 10% with increasing water supplied into the integrated system. When the S/C increases from 2 to 4, the rate of useful heat increases by 15%. As can be seen from Figure 5.15-(b), when the S/C increases from 2 to 4, the molar flow rate of CO₂ in the retentate stream increase by 38.5%, and thus, the total molar flow rate of the captured CO₂ increases by 4%. The depletion of methane in the system increases by 2.5%. Therefore, the methane conversion, hydrogen and CO₂ yields increase by 2.5%, 10%, and 4.8%, respectively. In addition, Table 10 shows the effects of the steam-to-carbon ratio on the exergy destruction rate of each component in the integrated system.

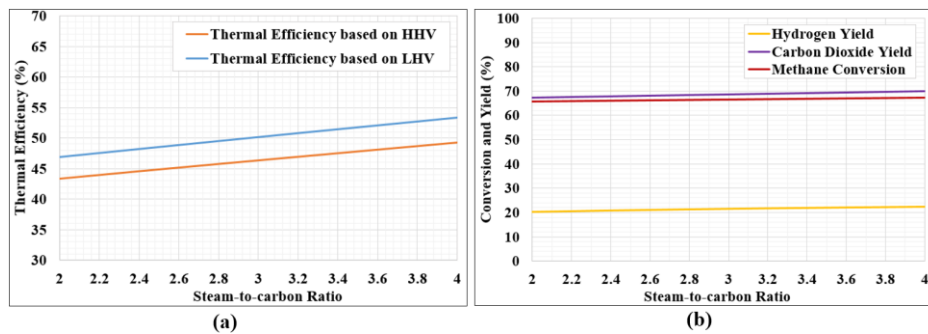


Figure 5.15 The change of; (a) thermal efficiency based on HHV and thermal efficiency based on LHV and (b) methane conversion, hydrogen yield, and CO₂ yield with the steam-to-carbon ratio in the MR

Table 5.15 The values of exergy destruction rate (W) of each component according to the steam-to-carbon ratio in the MR

S/C	Pump	Comp.	Mixer-1	Mixer-2	Burner
2	12.50	3.23×10^3	8.49×10^3	1.45×10^4	3.04×10^6
2.4	15	3.23×10^3	8.81×10^3	1.93×10^4	3.04×10^6
2.8	17.50	3.23×10^3	9.19×10^3	2.49×10^4	3.04×10^6
3.2	20	3.23×10^3	9.62×10^3	3.13×10^4	3.04×10^6
3.6	22.50	3.23×10^3	1×10^4	3.86×10^4	3.04×10^6
4	25	3.23×10^3	1.05×10^4	4.64×10^4	3.04×10^6
S/C	Boiler	MR	CO ₂ capture system	Air Valve	CH ₄ Valve
2	2.61×10^6	7.5×10^5	647.47	4.65×10^{-10}	4.54×10^{-13}
2.4	2.49×10^6	7.83×10^5	654.09	4.65×10^{-10}	4.54×10^{-13}
2.8	2.36×10^6	8.12×10^5	660.55	4.65×10^{-10}	4.54×10^{-13}
3.2	2.23×10^6	8.39×10^5	666.85	4.65×10^{-10}	4.54×10^{-13}
3.6	2.10×10^6	8.64×10^5	672.97	4.65×10^{-10}	4.54×10^{-13}
4	1.97×10^6	8.87×10^5	678.94	4.65×10^{-10}	4.54×10^{-13}

As can be seen from Table 5.15, when the S/C increases from 2 to 4, the exergy destruction rates of compressor, burner, air valve, and methane valve do not change, however, the exergy destruction rates of MR, water pump, Mixer-1, Mixer-2, and CO₂ capture system increase by 18%, 100%, 23.6%, 220%, and 4.8%, respectively; and that of the boiler decreases by 24.5%. Consequently, increasing the S/C increases the system performance. However, the rates of degradation of main components increases; and thus, the long-term stability of the integrated system is affected negatively.

5.4 Two-Dimensional Modeling Results

All 2-D models were developed using the COMSOL Multiphysics program. While developing 2-D modeling studies, 2-D modeling studies were carried out in different operating parameters and different membrane types (Pd-Ag and Pd-Au/Al₂O₃).

In this 2-D models, only the reaction and permeation sides where are found on the two sides of the membrane were investigated. The feed gas and sweep gas are fed from the same direction into the membrane reactor. Figure 5.16 shows the geometry used in the Study-1 and the Study-2.

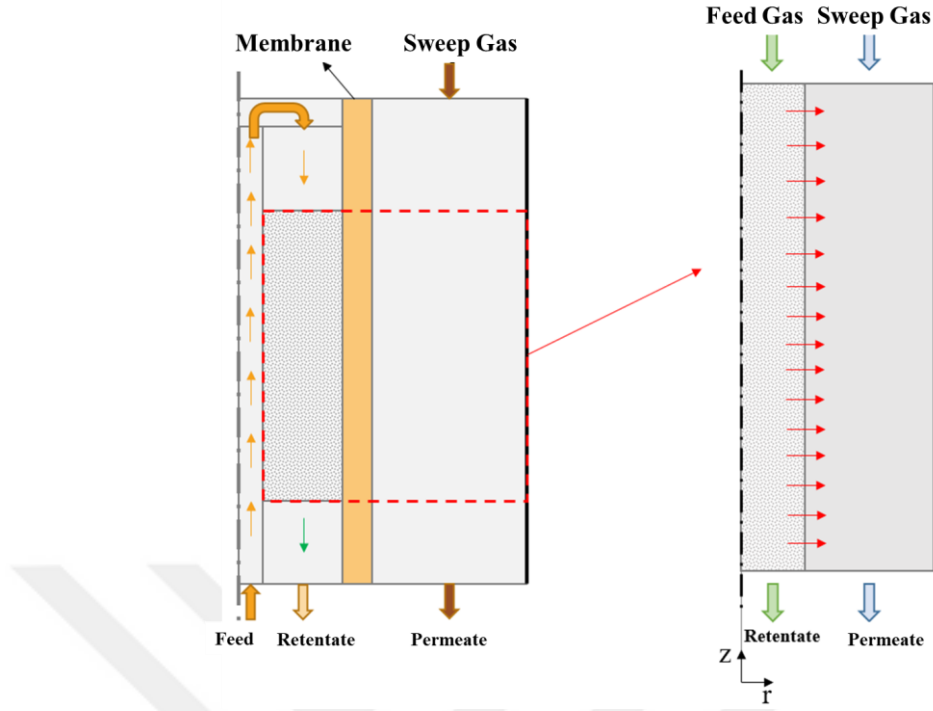


Figure 5.16 Geometry used in the Studies

The main assumptions are given as follows:

- In this model, two Transport of Concentrated Species physics (tcs) were used for the reaction and permeation sides to add two reaction sources. The inlet molar fractions of the species were given as input values in Transport of Concentrated Species physics. The tcs and tcs-2 physics were used for the reaction and permeation sides, respectively. Reaction sources for the reaction and permeation sides are given as follows:

$$Rxn_{source}^{reaction} = (3R_1 + R_2 + 4R_3)MW_{H_2} - m_{perm,H_2} \left(\frac{1}{r_{mem,out} - r_{mem,in}} \right) \quad (5.2)$$

$$Rxn_{source}^{permeation} = m_{perm,H_2} \left(\frac{1}{r_{mem,out} - r_{mem,in}} \right) \quad (5.3)$$

- The feed gas inlet pressure is given as the inlet condition in Darcy's law physics.
- In Heat Transfer in Fluid physics, the feed gas inlet temperature is given as the inlet condition. In addition, the constant temperature condition is used as the boundary condition on the wall.

5.4.1 Study 1- Distributions of Temperature, Molar Concentration, and Methane Conversion in the Reaction and Permeation Sides for Pd-Ag Membrane Reactor

In this study, the Pd-Ag membrane is used as the hydrogen perm-selective barrier placed between the reaction and the permeation sides. The geometric and operating parameters used in this study are given in Table 5.16.

Table 5.16 The geometric and operating parameters for the membrane reactor with Pd-Ag membrane

Parameter	Value
Inner diameter of membrane, $r_{i,i}$	0.9 cm
Outer diameter of membrane, $r_{i,o}$	1 cm
Inner diameter of reactor, $r_{o,i}$	3 cm
Outer diameter of reactor, $r_{o,o}$	8 cm
Reactor length	33 cm
Active layer length	10 cm
Mass of catalyst	3 g
Catalyst type	Rh(1%)/MgAl ₂ O ₄ /Al ₂ O ₃
Membrane type	Commercial self-supported Pd–Ag
Membrane thickness	150 μ m
Temperature of feed gas	25 °C
Temperature of permeate	400 °C
Permeation pressure	101.325 kPa
Reaction pressure	200 kPa
Pre-exponential factor for hydrogen flux calculation, $B_{H_2}^0$	8E–6 [mol·m/(m ² ·Pa·min)]
Activation energy for hydrogen flux calculation, E_m	14.8 kJ/mol
Inlet Mole fraction of CH ₄	0.0007 mol/min
Inlet Mole fraction of CO ₂	0.000401 mol/min
Inlet Mole fraction of H ₂ O	0.0021 mol/min
Inlet Mole fraction of H ₂	0
Inlet Mole fraction of CO	0

Figure 5.17, Figure 5.18, Figure 5.19, and Figure 5.20 show the distribution of molar concentration of all species except for hydrogen through the reaction side. As

you can see from Figures 5.17-5.20, the concentrations of methane and water decrease from 6.61 mol/m^3 to $1.42 \times 10^{-8} \text{ mol/m}^3$ and from 23.48 mol/m^3 to 8.75 mol/m^3 , respectively with the chemical reactions. The concentration of carbon monoxide first increases from 0.25 mol/m^3 to 0.36 mol/m^3 , then decreases to 0.025 mol/m^3 due to the water-gas shift reaction. The concentration of carbon dioxide increases from 11.56 mol/m^3 to 19.01 mol/m^3 with the water-gas shift reaction. Figure 5.21 shows the distribution of molar concentration of hydrogen through the reaction and permeation sides. As can be seen from Figure 5.21, the concentration of hydrogen on the reaction side firstly increases from 0.125 mol/m^3 to 0.32 mol/m^3 due to the chemical reactions and then decreases to 0.010 mol/m^3 due to the hydrogen permeation through the membrane. On the permeation side, the concentration of hydrogen increases from 0 to 0.12 mol/m^3 .

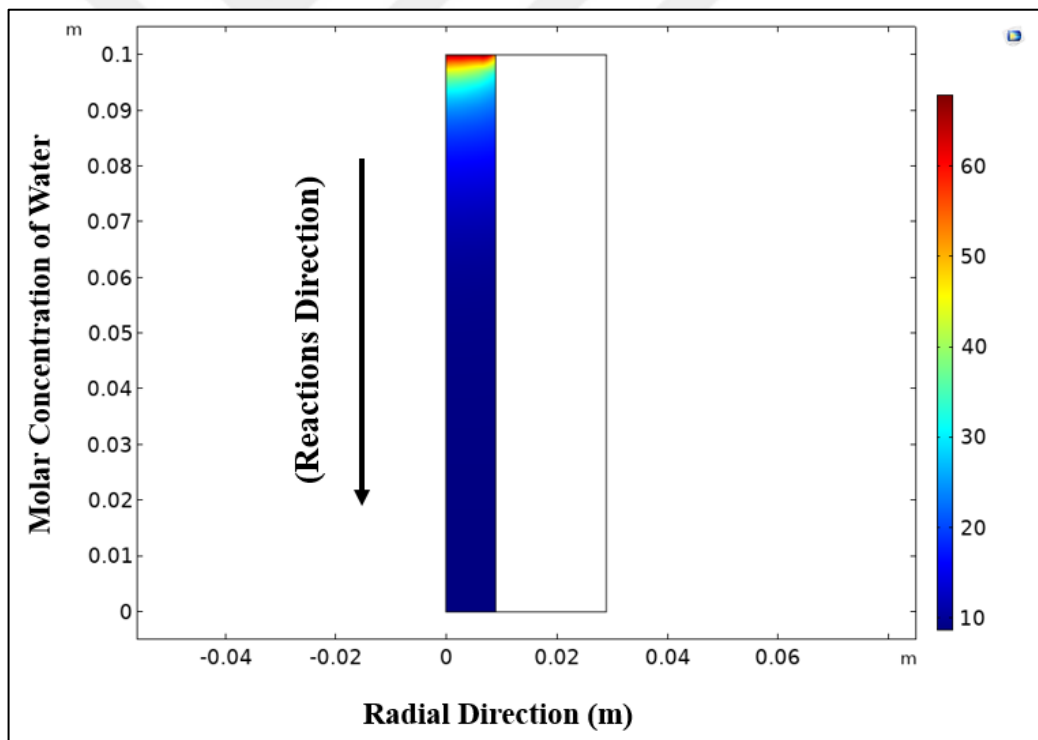


Figure 5.17 The distribution of molar concentration of H_2O through the reaction side at the 673 K

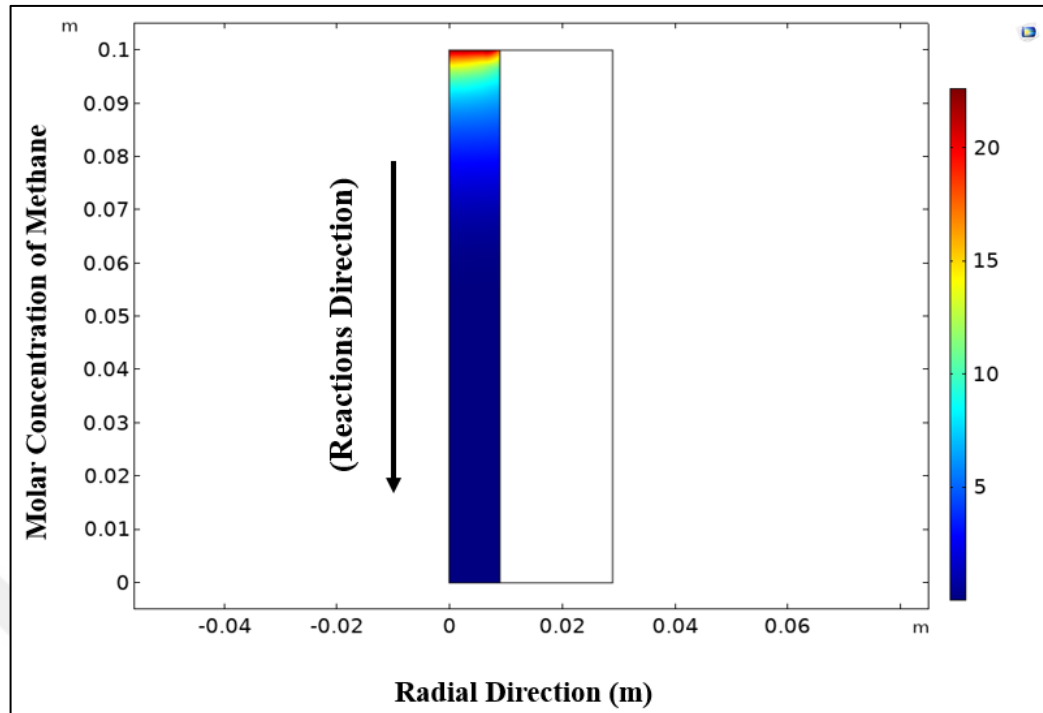


Figure 5.18 The distribution of molar concentration of CH_4 through the reaction side at the 673 K

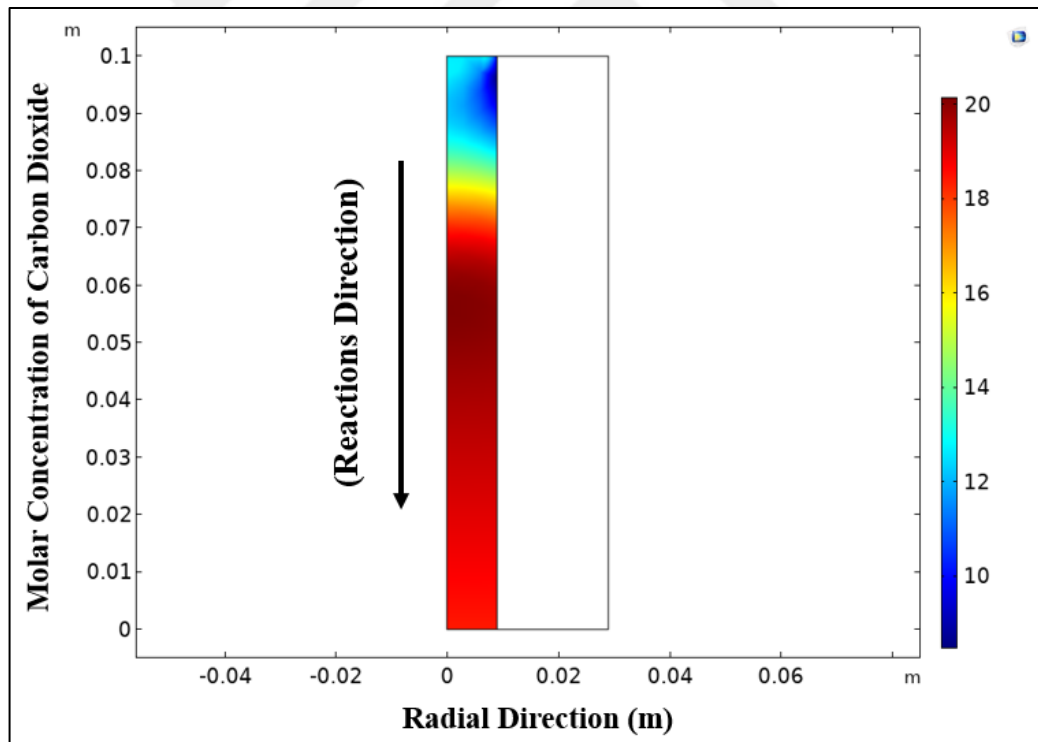


Figure 5.19 The distribution of molar concentration of CO_2 through the reaction side at the 673 K

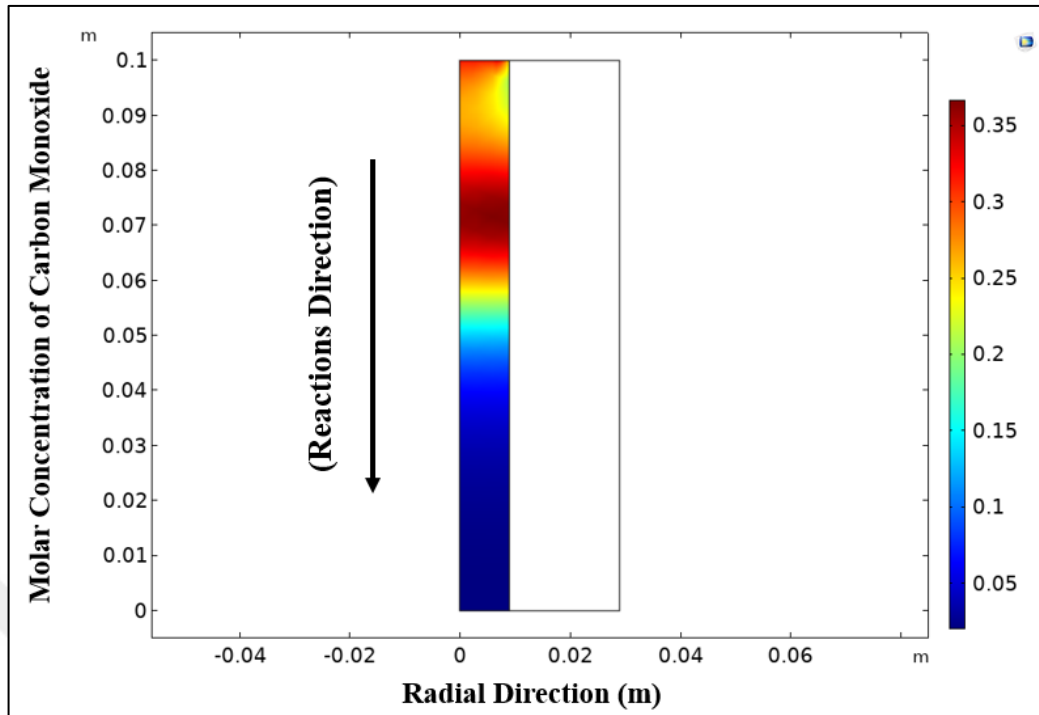


Figure 5.20 The distribution of molar concentration of CO through the reaction side at the 673 K

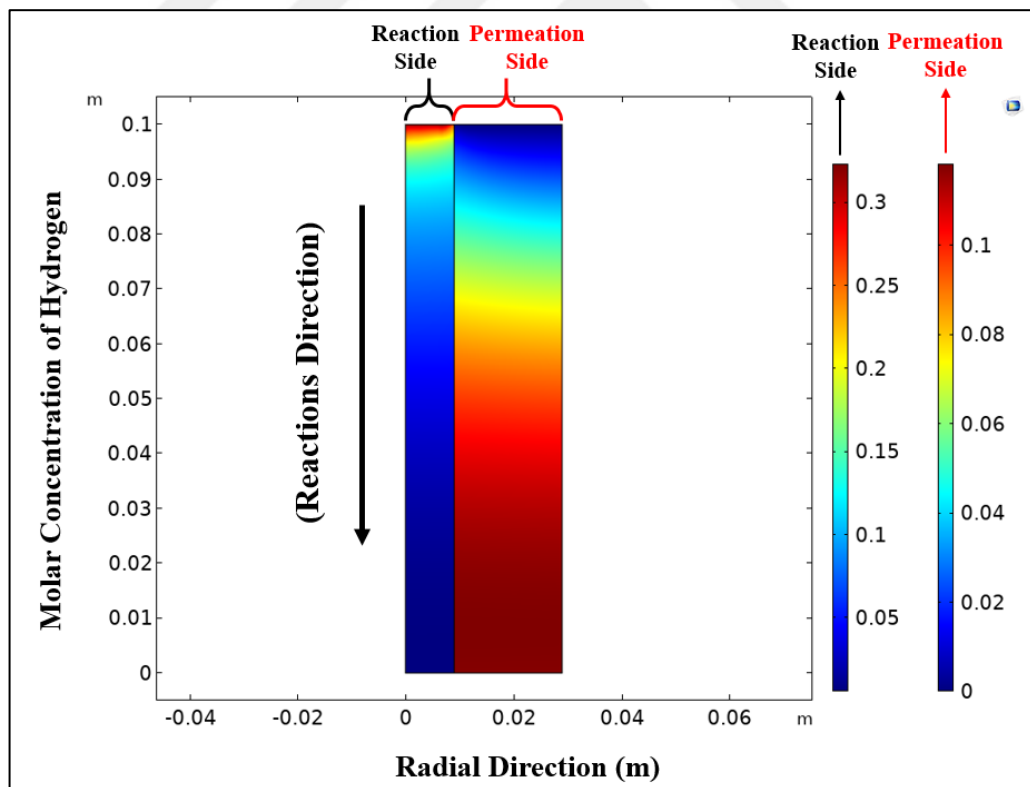


Figure 5.21 The distribution of molar concentration of hydrogen through the reaction and permeation sides at the 673 K

Figure 5.22 shows the temperature changes for the reaction and permeation sides through the axial and radial directions. In the reactor, the constant temperature assumption was used on the wall. The temperature distribution through the axial and radial directions on the permeation side increases from 611 K to 673 K. The temperature distribution through the axial and radial directions on the reaction side increases from 300 K to 672 K. The reason for the temperature increment on the reaction side can be explained by the chemical reactions.

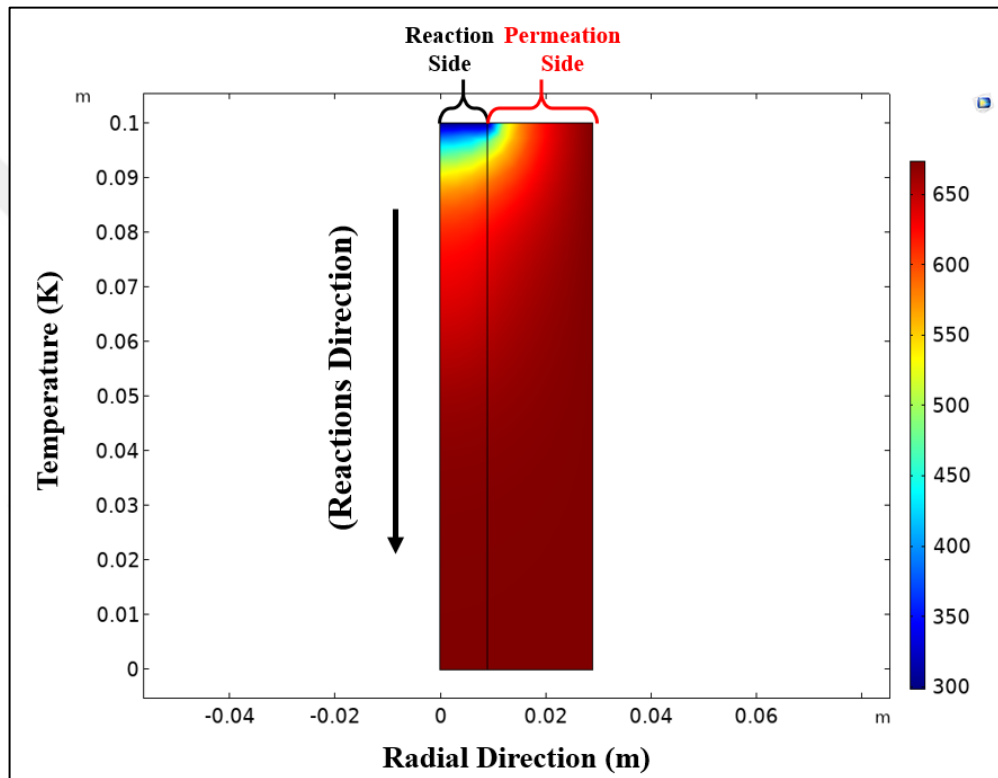


Figure 5.22 The distribution of temperatures for the reaction and permeation side through the axial and radial directions

Figure 5.23 shows the change of methane conversion through the axial and radial directions. The methane conversion value increases from 0 to 93%. In the membrane reactor, the methane in the feed gas is depleted in the first 4 cm and hydrogen is produced. This analysis can be shown that the active length of the membrane reactor can be shortened from 8 cm to 4 cm.

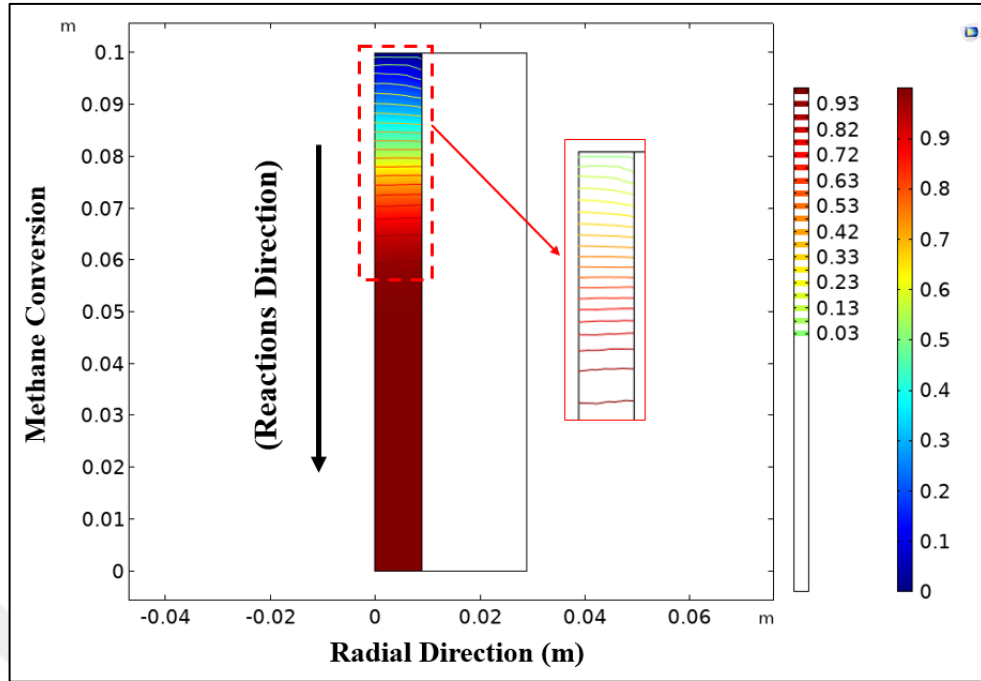


Figure 5.23 The distribution of methane conversion through the axial and radial directions

5.4.2 Study 2- Distributions of Temperature, Molar Concentration, and Methane Conversion in the Reaction and Permeation Sides for Pd–Au/Al₂O₃ Membrane Reactor

In this study, the Pd–Au/Al₂O₃ membrane is used as the hydrogen perm-selective barrier placed between the reaction and the permeation sides. The geometric and operating parameters used in this study are given in Table 5.17.

Figure 5.24, Figure 5.25, Figure 5.26, and Figure 5.27 show the distribution of molar concentration of all species except for hydrogen through the reaction side. As you can see from Figures 5.24-5.27, the concentrations of methane and water decrease from 2.16 mol/m³ to 1.07x10⁻⁶ and from 15.59 mol/m³ to 8.49 mol/m³, respectively with the chemical reactions. The concentration of carbon monoxide first increases from 0.58 mol/m³ to 0.63 mol/m³, then decreases to 0.074 mol/m³ due to the water-gas shift reaction. The concentration of carbon dioxide increases from 21.29 mol/m³ to 23.44 mol/m³ with the water-gas shift reaction, and then decreases to 17.91 mol/m³. Figure 5.28 shows the distribution of molar concentration of hydrogen through the reaction and permeation sides.

Table 5.17 The geometric and operating parameters for the membrane reactor with Pd–Au/Al₂O₃ membrane

Parameter	Value
Inner diameter of membrane, $r_{i,i}$	0.8 cm
Outer diameter of membrane, $r_{i,o}$	1 cm
Inner diameter of reactor, $r_{o,i}$	2.2 cm
Outer diameter of reactor, $r_{o,o}$	3 cm
Reactor length	8 cm
Active layer length	5 cm
Mass of catalyst	1.5 g
Catalyst type	Rh(1%)/MgAl ₂ O ₄ /Al ₂ O ₃
Membrane type	Non-commercial supported Pd–Au/Al ₂ O ₃
Membrane thickness	7 ÷ 8 μm
Temperature of feed gas	25 °C
Temperature of permeate	550 °C
Permeation pressure	101.325 kPa
Reaction pressure	150 kPa
Pre-exponential factor for hydrogen flux calculation, $B_{H_2}^0$	5.09E–9 [mol·m/(m ² ·Pa·min)]
Activation energy for hydrogen flux calculation, E_m	12.1 kJ/mol
Inlet Mole fraction of CH ₄	0.0007 mol/min
Inlet Mole fraction of CO ₂	0.000401 mol/min
Inlet Mole fraction of H ₂ O	0.0021 mol/min
Inlet Mole fraction of H ₂	0
Inlet Mole fraction of CO	0

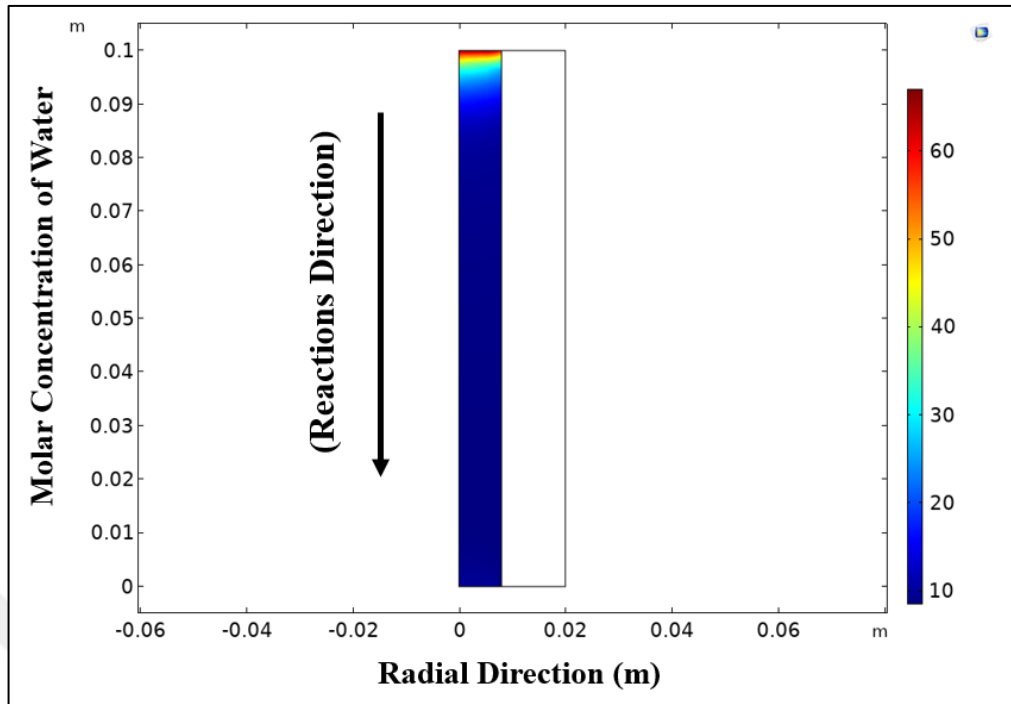


Figure 5.24 The distribution of molar concentration of H_2O through the reaction side at the 823 K

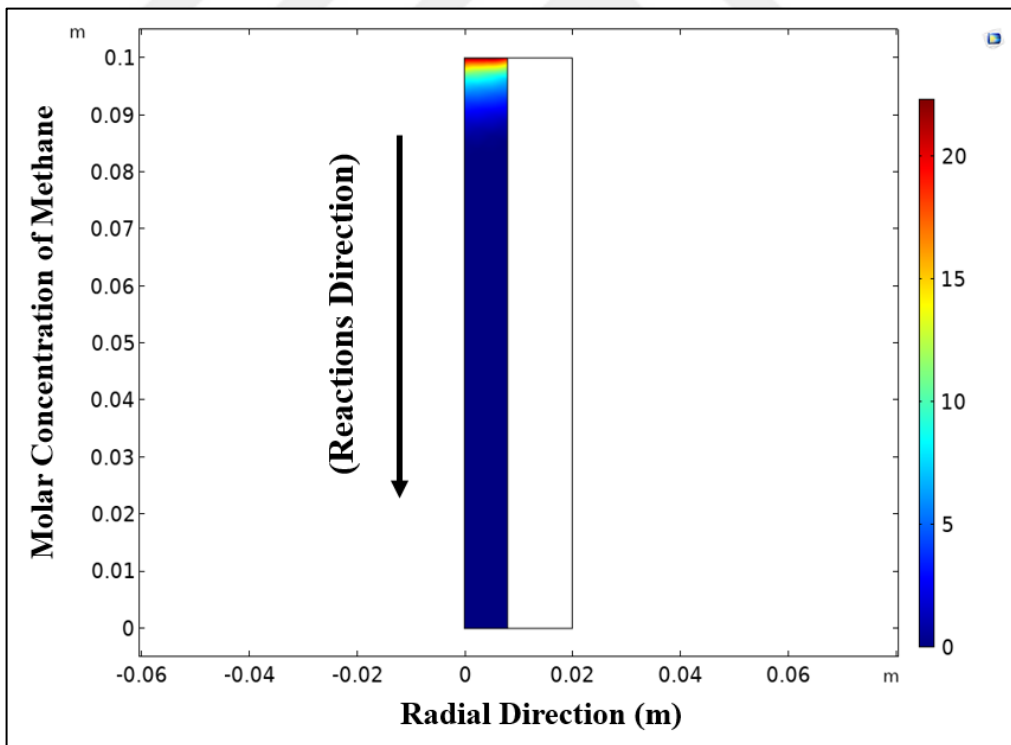


Figure 5.25 The distribution of molar concentration of CH_4 through the reaction side at the 823 K

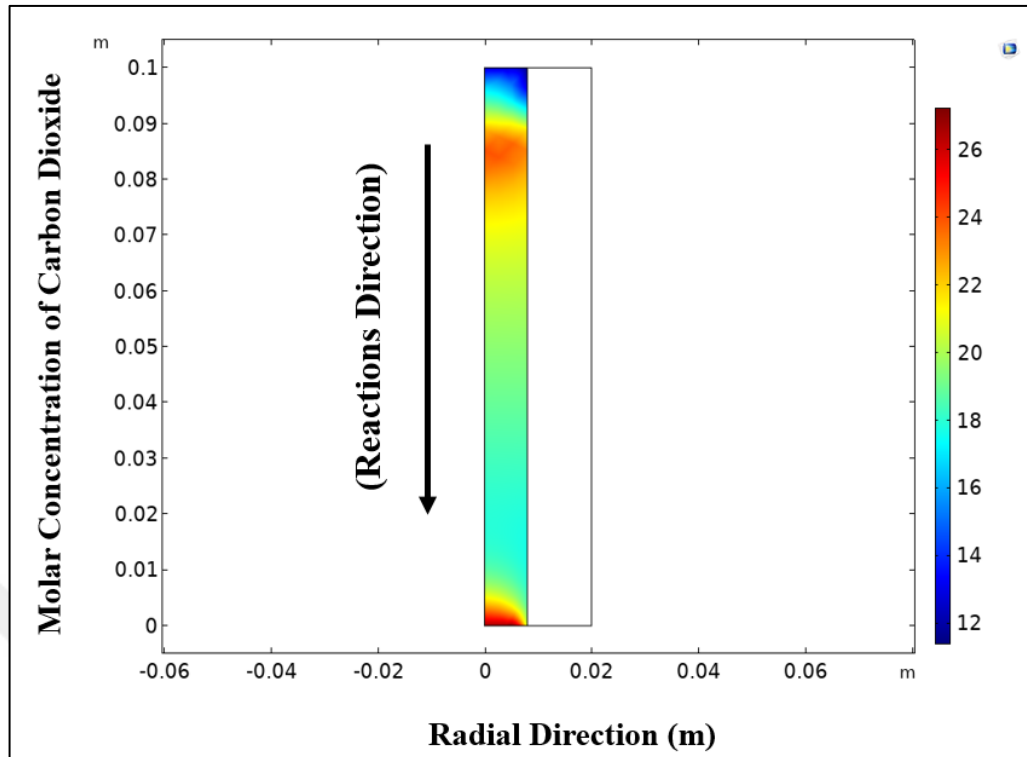


Figure 5.26 The distribution of molar concentration of CO_2 through the reaction side at the 823 K

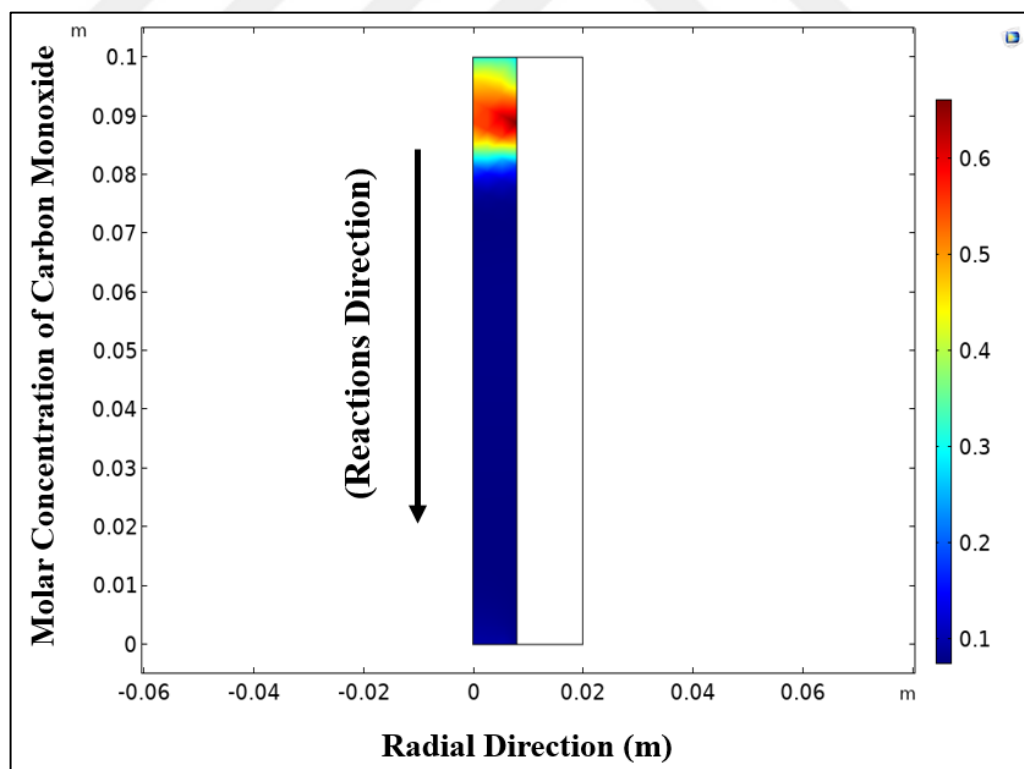


Figure 5.27 The distribution of molar concentration of CO through the reaction side at the 823 K

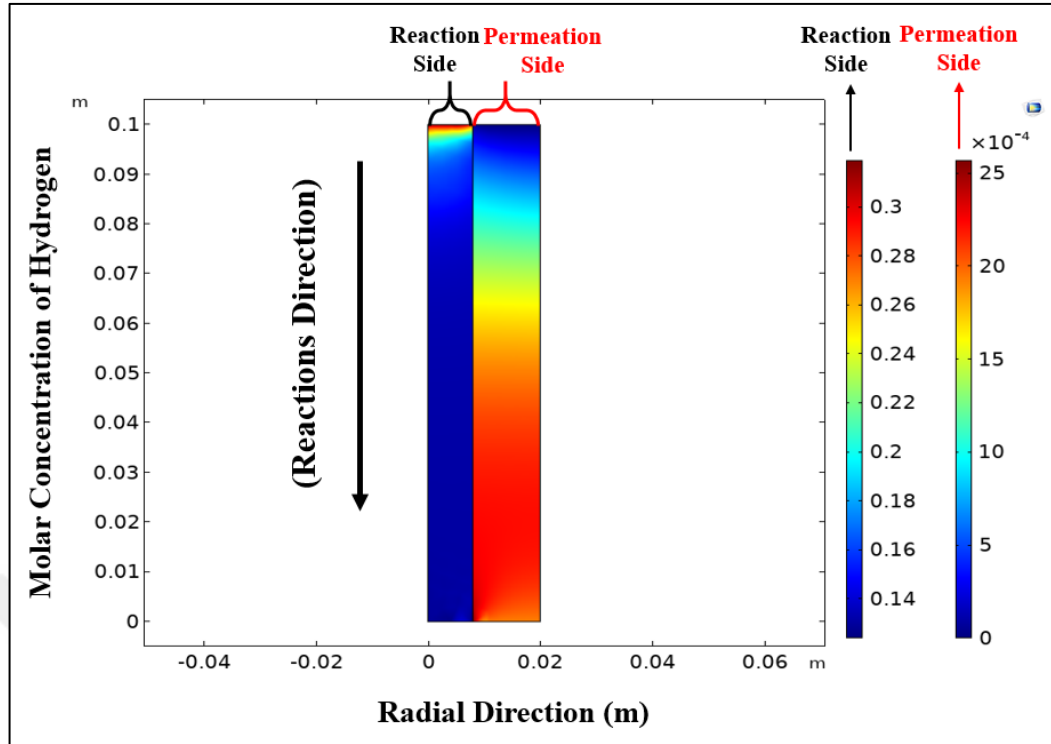


Figure 5.28 The distribution of molar concentration of hydrogen through the reaction and permeation sides at the 823 K

As can be seen from Figure 5.28, the concentration of hydrogen on the reaction side firstly increases from 0.15 mol/m^3 to 0.30 mol/m^3 due to the chemical reactions and then decreases to 0.13 mol/m^3 due to the hydrogen permeation through the membrane. On the permeation side, the concentration of hydrogen increases from 0 to 0.002 mol/m^3 . When Study-1 and Study-2 were compared, the molar concentration of the permeated hydrogen for Study-2 was less found. The reason can be explained that in self-supported membranes (Pd-Ag), almost all of the hydrogen produced on the reaction side passes through the membrane to the permeation side. However, in supported membranes (Pd-Au/ Al_2O_3), a small part of the hydrogen can pass, since the membrane thickness is reduced for cost reasons and reinforced with the support material.

Figure 5.29 shows the temperature changes for the reaction and permeation sides through the axial and radial directions. In the reactor, the constant temperature assumption was used on the wall. The temperature distribution through the axial and radial directions on the permeation side increases from 741 K to 823 K. The

temperature distribution through the axial and radial directions on the reaction side increases from 300 K to 823 K. The reason for the temperature increment on the reaction side can be explained by the chemical reactions.

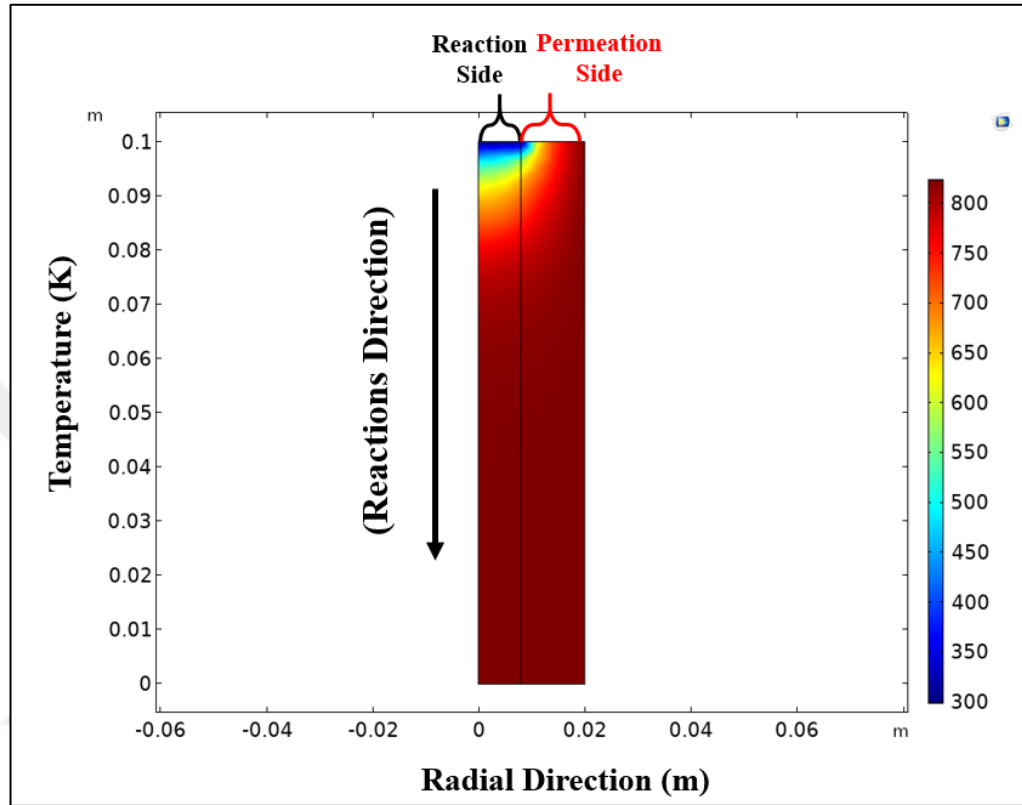


Figure 5.29 The distribution of temperatures for the reaction and permeation side through the axial and radial directions

Figure 5.30 shows the change of methane conversion through the axial and radial directions. The methane conversion value increases from 0 to 97%. In the membrane reactor, the methane in the feed gas is depleted in the first 2 cm and hydrogen is produced. This analysis can be shown that the active length of the membrane reactor can be shortened from 5 cm to 2 cm.

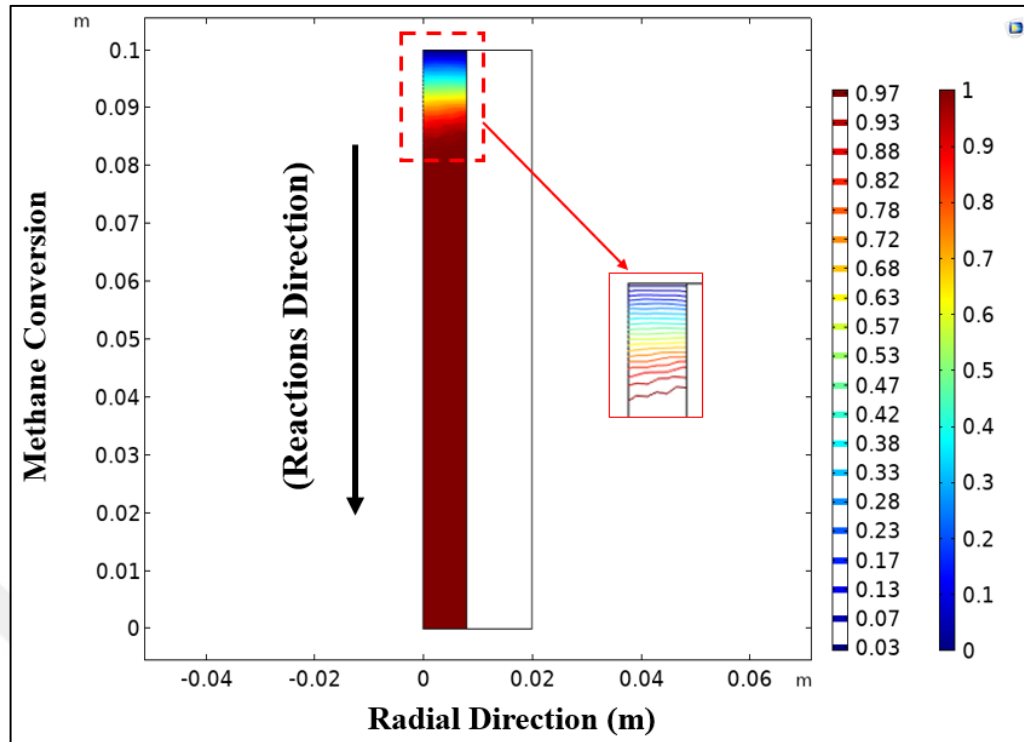


Figure 5.30 The distribution of methane conversion through the axial and radial directions

CHAPTER SIX

CONCLUSIONS

In this thesis, the mathematical modeling method is used to improve the performance of the membrane reactor providing hydrogen production from biogas. Using the MATLAB program, 1-D models of a membrane reactor were created according to two different case study analyses and validated separately with the results of two reference studies in the literature. According to the first case study analysis, the temperature distributions for both the permeation and the reaction sides of the reactor were investigated with the developed 1-D membrane reactor model. In addition, the changes in molar flow rates of all species, methane conversion, and hydrogen recovery along the reactor length were investigated. According to the second case study analysis, the temperature distributions for both the permeation and the reaction sides of the reactor were investigated similarly using the developed 1-D membrane reactor model. In addition, parametric analysis of operating temperature, reaction pressure, and steam to carbon ratio parameters on methane conversion and hydrogen recovery were realized. The 1-D membrane reactor model developed in the first case study was integrated into an integrated system consisting of CO₂ capture and various plant components (compressor, boiler, burner, pump, blower, and two mixers) and the system-level model was developed in the MATLAB program, using principles of electrochemistry (reaction kinetics) and thermodynamics (energy and exergy analysis). The changes in the molar flow rates of each species and the temperature along the reactor length were investigated. The effects of some operating parameters (operating temperature, steam-carbon ratio, and reaction pressure) on system performance (methane conversion, hydrogen yield, CO₂ efficiency, and thermal efficiency (based on LHV and HHV)) were investigated. In addition, the exergy destruction rates of each component in the integrated system and the exergy destruction rate (W) values of each component according to the change of these parameters were examined. Moreover, in order to validate the developed mathematical models, an experimental setup that enables the production of hydrogen from biogas with a membrane reactor was set up and the experimental studies were realized at the Membrane Technology Institute in Italy. However, due to the technical problems

experienced there, only calibration and permeability tests of the Pd/Al₂O₃ membrane separator module were carried out. Finally, 2-D membrane reactor models were developed using COMSOL Multiphysics software to investigate the behavior of the reactor through both the axial and radial directions. In 2-D models, four physics (transport concentrated species, darcy's law, heat transfer in fluid, and chemistry) were used to define mass, energy, and reaction kinetics values.

The main findings derived from the detailed literature survey about membrane reactors and their modeling are as follows:

- The most used reaction rate expression for the steam-methane reforming reactions has been the one proposed by Xu and Froment (1989). In the recent modeling studies, other researchers have followed their study and formed their kinetic expressions.
- The studies on the mathematical modeling of a MR have not included detailed modeling of hydrogen permeation through a membrane that consists of the external mass transfer, adsorption and desorption, dissolution and association, diffusion, and mass transport in porous support. Generally, the hydrogen permeation flux has been calculated using Sieverts' law.
- 1-D MR models have been generally examined according to the pseudo-homogeneous approach, whereas the heterogeneous approach has been used in 2-D models.
- In 2-D modeling, for the reaction side, the mass and energy balance equations in the radial and axial directions have been generally included, however the momentum balance equation only in the axial direction has been considered. On the other hand, for the permeation side, the mass and energy balance equations have been generally included in the axial direction.
- Although 3-D MR models are supposed to be more accurate and give more insights compared to 1-D and 2-D models, according to authors' knowledge, no studies on the 3-D models of MR providing hydrogen production from methane exist in the literature.

The main findings derived from the 1-D models of membrane reactor for Case Study-1 and Case Study-2 are as follows:

- In the first analysis, when the results of the one-dimensional model in Case study-1 were compared with the reference study, the error percentages for the methane conversion, hydrogen recovery, retentate temperature, and permeate temperature were calculated as 73.68%, 13.84%, 12.18%, and 8.43%, respectively. After the solution algorithm of this 1-D model of membrane reactor used in Case Study-1 was improved, the error values for the methane conversion, the hydrogen recovery, the retentate temperature, and the permeate temperature decreases to 0.26%, 7.69%, 0.24%, and 0.86%, respectively.
- In Case study-2, after the genetic algorithm method, the error percentages for methane conversion and hydrogen recovery are calculated as 1.92% and 1.14%, respectively. Thus, the methane conversion and the hydrogen recovery values at 400°C and 1.2 SF depending on the changing reaction pressure (1, 2, and 3 bar) were investigated by using the calculated variables from the genetic algorithm method. The results showed that hydrogen recovery values are relatively validated, whereas the methane conversion values are not validated when the results are compared with the experimental results.

The main findings derived from the experimental studies conducted in the Institute of Membrane Technologies (CNR-ITM) in Italy are as follows:

- When the permeation test for hydrogen was performed in experimental studies, the regression coefficients were 0.99163, 0.99159, 0.9912, 0.9905, 0.9893, and 0.9878 with n values of 1, 0.9, 0.8, 0.7, 0.6 and 0.5, respectively. When the regression coefficients were examined, the closest value to 100% was found for n=1. If the n value is equal to 1, it shows that the surface controls are more dominant than diffusion, thus the most effective mechanism was found as the Knudsen diffusion mechanism.
- As a result of the experimental study, the ideal selectivity values of H_2/CH_4 , H_2/CO_2 and H_2/N_2 were calculated as 58.52, 94.19 and 65.57, respectively, according to varying pressures. Since the membrane used in the experiments was a supported membrane (composite membrane), not only hydrogen but also other gases passed

through the membrane. For this reason, the ideal selectivity of hydrogen was calculated to be lower than that of self-supporting membranes.

The main findings derived from the integrated system level model including membrane reactor + CO₂ capture system to generate decarbonized hydrogen are as follows:

- When the results of a 1-D MR model are compared with the results of the reference study (Alavi et al., 2017), the error values for the outlet reaction temperature, the outlet permeate temperature, the methane conversion, and the hydrogen recovery are calculated as 0.24%, 0.25%, 0.32 %, and 6.04%, respectively. These error values can be accepted for validation.
- When the operating temperature of MR increases from 673 K to 823 K, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the system increase by 7.5% and 6.6% respectively. In addition, the methane conversion, hydrogen yield and CO₂ yield increase by 5%, 53.7% and 4.8%, respectively, with the same amount of increase in the operating temperature.
- When the inlet pressure of feed gas in the MR increases from 5 bar to 15 bar, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the system increase by 4.1% and 3.7%, respectively. In addition, the increase in the hydrogen yield can be calculated as 44.84%; whereas the CO₂ yield and methane conversion are constant with the same amount of increase in the reaction pressure of MR.
- When the S/C increases from 2 to 4, the thermal efficiency based on HHV and the thermal efficiency based on LHV of the overall system increase by 13.6% and 13.7%, respectively. In addition, the methane conversion, hydrogen yield and CO₂ yield increase by 2.5%, 10%, and 4.8%, respectively, with the same amount of increase in the S/C.
- The most influential parameter which affects the thermal efficiencies of the system is the S/C, whereas the most influential parameter which affects the hydrogen yield of the system is the operating temperature. Methane conversion and CO₂ yield are the least affected parameter. The most influential variable which is affected by the parameters is the hydrogen yield.

- The exergy destruction rate of the burner is the highest with 49%, which is followed by the boiler with 36%, and then by the MR with 14%.
- When the exergy destruction rates of main components (burner, boiler, and MR) are investigated with the changing of operating parameters, the exergy destruction rate of the burner keeps constant. The exergy destruction rate of the boiler decreases with the changes in the operating temperature and S/C; while it keeps constant with the change in the reaction pressure. The exergy destruction of MR according to the change in the operating temperature, the reaction pressure, and S/C increases by 66%, 46%, and 18%, respectively. Consequently, the rates of degradation of MR increases; and thus, the long-term stability of the integrated system is affected negatively.
- At the baseline simulation conditions (773 K, 9 bar, and 3 S/C), thermal efficiency based on HHV, thermal efficiency based on LHV, methane conversion of the system, hydrogen yield, and CO₂ yield are calculated as 47%, 51%, 67%, 22%, and 66%, respectively.

The main findings derived from the 2-D membrane reactor models are as follows:

- When the results of the 2-D reaction side model (Study-1) are examined, it is observed that the trends of the distributions of temperature and molar fractions are similar to the results of the 1-D reaction side model, however the amount of temperature change was found as different due to the radial effect.
- In the 2-D model of the self-supported Pd-Ag membrane reactor given in Study-1, the concentrations of methane and water decrease from 6.61 mol/m³ to 1.42x10⁻⁸ and from 23.48 mol/m³ to 8.75 mol/m³, respectively with the chemical reactions. The concentration of carbon monoxide first increases from 0.25 mol/m³ to 0.36 mol/m³, then decreases to 0.025 mol/m³ due to the water-gas shift reaction. The concentration of carbon dioxide increases from 11.56 mol/m³ to 19.01 mol/m³ with the water-gas shift reaction. The concentration of hydrogen on the reaction side firstly increases from 0.125 mol/m³ to 0.32 mol/m³ due to the chemical reactions and then decreases to 0.010 mol/m³ due to the hydrogen permeation through the membrane. On the permeation side, the concentration of hydrogen increases from 0 to 0.12 mol/m³. The temperature distribution through the axial and radial

directions on the permeation side increases from 611 K to 673 K. The temperature distribution through the axial and radial directions on the reaction side increases from 300 K to 672 K. Moreover, the methane conversion value increases from 0 to 93%. In the membrane reactor, the methane in the feed gas is depleted in the first 4 cm and hydrogen is produced. This analysis can be shown that the active length of the membrane reactor can be shortened from 8 cm to 4 cm.

- In the 2-D model of the supported Pd-Au/Al₂O₃ membrane reactor given in Study-2, the concentrations of methane and water decrease from 2.16 mol/m³ to 1.07x10⁻⁶ and from 15.59 mol/m³ to 8.49 mol/m³, respectively with the chemical reactions. The concentration of carbon monoxide first increases from 0.58 mol/m³ to 0.63 mol/m³, then decreases to 0.074 mol/m³ due to the water-gas shift reaction. The concentration of carbon dioxide increases from 21.29 mol/m³ to 23.44 mol/m³ with the water-gas shift reaction and then decreases to 17.91 mol/m³. The concentration of hydrogen on the reaction side firstly increases from 0.15 mol/m³ to 0.30 mol/m³ due to the chemical reactions and then decreases to 0.13 mol/m³ due to the hydrogen permeation through the membrane. On the permeation side, the concentration of hydrogen increases from 0 to 0.002 mol/m³. The temperature distribution through the axial and radial directions on the permeation side increases from 741 K to 823 K. The temperature distribution through the axial and radial directions on the reaction side increases from 300 K to 823 K. Moreover, The methane conversion value increases from 0 to 97%. In the membrane reactor, the methane in the feed gas is depleted in the first 2 cm and hydrogen is produced. This analysis can be shown that the active length of the membrane reactor can be shortened from 5 cm to 2 cm.
- When Study-1 and Study-2 were compared, the molar concentration of the permeated hydrogen for Study-2 was less found. The reason can be explained that in self-supported membranes (Pd-Ag), almost all of the hydrogen produced on the reaction side passes through the membrane to the permeation side. However, in supported membranes (Pd-Au/Al₂O₃), a small part of the hydrogen can pass, since the membrane thickness is reduced for cost reasons and reinforced with the support material.

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