

Article

Not peer-reviewed version

Numerical Analysis on Impact of Membrane Thickness and Temperature on Characteristics of Biogas Dry Reforming Membrane Reactor Using Pd/Cu Membrane and Ni/Cr Catalyst

[Akira Nishimura](#)^{*}, Ryoma Ichii, Souta Yamada, [Mizuki Ichikawa](#), Taisei Hayakawa, [Eric Hu](#)

Posted Date: 7 January 2025

doi: 10.20944/preprints202501.0403.v1

Keywords: biogas dry reforming; membrane reactor; numerical simulation; thickness of membrane; Ni/Cr catalyst



Preprints.org is a free multidisciplinary platform providing preprint service that is dedicated to making early versions of research outputs permanently available and citable. Preprints posted at Preprints.org appear in Web of Science, Crossref, Google Scholar, Scilit, Europe PMC.

Copyright: This open access article is published under a Creative Commons CC BY 4.0 license, which permit the free download, distribution, and reuse, provided that the author and preprint are cited in any reuse.

Article

Numerical Analysis on Impact of Membrane Thickness and Temperature on Characteristics of Biogas Dry Reforming Membrane Reactor Using Pd/Cu Membrane and Ni/Cr Catalyst

Akira Nishimura ^{1,*}, Ryoma Ichii ¹, Souta Yamada ¹, Mizuki Ichikawa ¹, Taisei Hayakawa ¹ and Eric Hu ²

¹ Division of Mechanical Engineering, Mie University, Tsu 514-8507, Japan; 424M107@m.mie-u.ac.jp (R.I.); 423M161@m.mie-u.ac.jp (S.Y.); 424M108@m.mie-u.ac.jp (M.I.); 421027@m.mie-u.ac.jp (T.H.)

² School of Engineering, the University of Adelaide, Adelaide, SA 5005, Australia; eric.hu@adelaide.edu.au

* Correspondence: nisimura@mach.mie-u.ac.jp; +81-59-231-9747

Abstract: The aim of this study is to clarify the characteristics of BDR in the membrane reactor using Pd/Cu membrane and Ni/Cr catalyst by the numerical simulation. This study has conducted the numerical simulation using the CFD software COMSOL Multiphysics ver. 6.2. The impact of the initial reaction temperature and the thickness of Pd/Cu membrane on the characteristics of BDR in the membrane reactor using Pd/Cu membrane and Ni/Cr catalyst is also investigated. The initial reaction temperature is changed by 400 °C, 500 °C and 600 °C and the thickness of Pd/Cu membrane is changed by 20 µm, 40 µm and 60 µm. The molar concentrations of CH₄ and CO₂ decrease with the increase in the initial reaction temperature, while the molar concentrations of H₂, CO, H₂O and C increase with the increase in the initial reaction temperature. In addition, the molar concentrations of H₂ in reaction chamber, Pd/Cu membrane and sweep chamber increase with the increase in the initial reaction temperature. Moreover, the molar concentrations of H₂ in Pd/Cu membrane and sweep chamber increase with the decrease in the thickness of Pd/Cu membrane. It is revealed that CH₄ conversion, CO₂ conversion and H₂ yield increase with the increase in the initial reaction temperature as well as the decrease in the thickness of Pd/Cu membrane.

Keywords: biogas dry reforming; membrane reactor; numerical simulation; thickness of membrane; Ni/Cr catalyst

1. Introduction

Green H₂ is one of promising procedure to solve the global warming problem. Though there is a lot of technology to produce green H₂, this study focuses on a biogas dry reforming (BDR) as a technology to produce green H₂. A biogas is a fuel consisting of CH₄ (55-75 vol%) and CO₂ (25-45 vol%) [1], generally. A biogas is produced from fermentation by the action of anaerobic microorganisms on raw materials, e.g., garbage, livestock excretion, and sewage sludge. 1.46 EJ of biogas gas produced in the world in 2020, which was five times as large as that in 2000 [2]. Consequently, it can be expected that the amount of produced biogas increases more in the near future.

A biogas is generally used as a fuel for gas engines and micro gas turbines [3]. However, the power output is lower compared to using a natural gas as a fuel since the heating value is lower due to including CO₂. This study has suggested the combination system consisting of a BDR reactor with a solid oxide fuel cell (SOFC) to solve this problem [4–6]. CO which is a by-product from BDR can be utilized as a fuel for SOFC. The total energy conversion efficiency is higher than the existing power

generation systems, i.e., gas engines and micro gas turbines since SOFC can be a co-generation system.

There are many reported researches on BDR recently [7–14]. The development of catalyst is one subject to improve the performance of BDR. From the literature survey, this study can claim that Ni-based catalysts have been investigated for BDR [7–14]. Ni/Ce/Al was developed and performed of the CH₄ conversion of 65 – 79 % and the CO₂ conversion of 77 – 86 % at 750 °C [7]. La/Ni/SBA-16 exhibited the CH₄ conversion of 86 % and the CO₂ conversion of 92 % at 700 °C [8]. The CH₄ conversion and the CO₂ conversion increased with the increase in the reaction temperature from 600 °C to 700 °C. Ni/CeO₂/Al₂O₃ performed the CH₄ conversion of approximately 100 % and the CO₂ conversion of approximately 100 % at 800 °C [9]. Ni/ γ -Al₂O₃ exhibited the CH₄ conversion of 90 % and the CO₂ conversion of 50 % at 800 °C [10]. Ni/CeZrO₂ performed the CH₄ conversion of approximately 40 % and the CO₂ conversion of approximately 55 % at 800 °C [11]. The CH₄ conversion and the CO₂ conversion increased with the increase in the reaction temperature from 500 °C to 800 °C. Ni/Al₂O₃ exhibited the CH₄ conversion of approximately 70 % and the CO₂ conversion of approximately 70 % at 700 °C [12]. Ni/La/Ti performed the CH₄ conversion of approximately 100 % and the CO₂ conversion of approximately 100 % at 800 °C [13]. The CH₄ conversion and the CO₂ conversion increased from 600 °C to 800 °C where they increased from approximately 78 % to 100 % and from approximately 55 % to 100 %, respectively. The thermogravimetric analysis for Ni/Cao/Al₂O₃ was investigated, which clarified the effect of heating rate on the H₂ production rate considering some chemical reaction schemes [14]. When the heating rate increased from 5 K/min to 20 K/min, the maximum H₂ production rate rose from 7×10^{-5} mol/s to 1×10^{-4} mol/s.

Though several Ni-based catalysts have been investigated, the Ni/Cr catalyst has not been examined well without authors' previous studies [5,15].

In addition, this study thinks it is important to operate at lower temperature in order to improve the thermal energy efficiency of BDR, resulting that BDR is an endothermic reaction. We think a membrane reactor is an effective procedure to match this purpose since the H₂ production rate of BDR is promoted by providing the non-equilibrium state with H₂ separation from the reaction site of catalyst [5]. Pd is known as a material of H₂ separation membrane [16]. The permeation of H₂ from a high to a low partial pressure region occurs in the following several stages: (a) dissociative adsorption of H₂ on the gas-metal interface; (b) sorption of the atomic H₂ into the bulk metal; (c) diffusion of atomic H₂ through the bulk metal membrane; (d) recombination of atomic H₂ to form H₂ molecules at the interface metal/gas permeate; (e) desorption of molecular H₂ [16]. Since the cost of pure H₂ is expensive, several Pd alloys are considered as a material of H₂ separation membrane. Though several Pd alloy membranes such as Pd/Ag and Pd/Au are commercialized as well as used for the research works, the cost of Pd/Cu is relatively smaller compared to that of Pd/Ag, Pd/Au and pure Pd. We think the cost is important factor to apply the proposed system to the industry in the near future. Therefore, this study selects the Pd/Cu as H₂ separation membrane. It is reported that Pd/Cu was used for H₂ separation membrane used for the previous study [17]. The commercial catalysts such as Al₂O₃, Cr₂O₃, CrO₃ and CuO were used for a water gas shift reaction (WGS) in the study. The increase in the conversion rate increased with the steam/carbon ratio from 1 to 3 and became smooth from 4 to 5. The membrane reactor using Pd/Cu membrane and Ni/Cu catalyst was investigated by the previous study conducted by the authors of this study experimentally [5]. Though the numerical study on BDR using Ni/Cr catalyst in the rectangular reactor was conducted by the authors of this study [15], the numerical study to clarify the characteristics of BDR conducted in the membrane reactor using Pd/Cu membrane and Ni/Cu catalyst has not been investigated yet.

Therefore, the aim of this study is to clarify the characteristics of BDR in the membrane reactor using Pd/Cu membrane and Ni/Cr catalyst by the numerical simulation. This study conducts the numerical simulation using the CFD software COMSOL Multiphysics ver. 6.2. Since there are many

previous studies using COMSOL Multiphysics for the numerical simulation of BDR on reaction characteristic as well as heat and mass transfer [18–21], this study has adopted COMSOL Multiphysics for the numerical analysis in this study. The impact of the initial reaction temperature and the thickness of Pd/Cu membrane on the characteristics of BDR in the membrane reactor using Pd/Cu membrane and Ni/Cr catalyst is also investigated. The initial reaction temperature is changed by 400 °C, 500 °C and 600 °C. The thickness of Pd/Cu membrane is changed by 20 µm, 40 µm and 60 µm. 2D model which simulates the membrane reactor used in the authors' previous studies [4,5] is adopted in order to short the calculation time though the actual experimental reactors 3D. The molar ratio of CH₄:CO₂ is set 1.5:1, which simulates a biogas in this study. To investigate the initial reaction temperature and the thickness of Pd/Cu membrane on the characteristics of BDR including the other reactions, the following reactions are considered:

<Dry reforming (DR)>



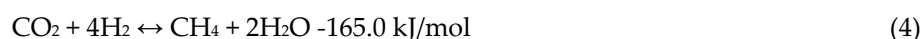
<Steam reforming (SR)>



<Reverse water gas shift reaction (RWGS)>



<Methanation reaction (MR)>



<Methane decomposition reaction (MDR)>



<Boudouard reaction (BD)>



2. Numerical Simulation Procedure of BDR Membrane Reactor Using Pd/Cu Membrane and Ni/Cr Catalyst

2.1. A Mathematical Formation

This study conducted the numerical simulation by a commercial multi-physics software, COMSOL Multiphysics, ver. 6.2. As to COMSOL Multiphysics, we can select to customize various partial differential equations and combine to achieve direct coupled multi-physics field analysis easily [22]. COMSOL Multiphysics has simulation function codes. The following governing equations are involved in COMSOL Multiphysics.

The equations of mass conservation in porous material can be defined as following:

$$\vec{u} = -\frac{\kappa}{\mu}(\nabla p + \rho g \nabla D) \quad (7)$$

$$\nabla \cdot (\rho \vec{u}) = Q_m \quad (8)$$

$$\nabla \cdot \rho \left[-\frac{\kappa}{\mu}(\nabla p) \right] = Q_m \quad (9)$$

where $\vec{u}$ means a velocity vector [m/s], κ means a permeability [m²], μ indicates a viscosity [Pa·s], ρ indicates a density [kg/m³], g indicates a gravitational acceleration [m/s²], D indicates a height [m], and Q_m indicates a mass source term [kg/(m³·s)].

The equation of momentum conservation in porous material can be defined by the Brinkmann equation, as following:

$$\frac{\rho}{\varepsilon_p} \left(\vec{u} \cdot \nabla \right) \frac{\vec{u}}{\varepsilon_p} = -\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon_p} \left\{ \mu \left(\nabla \vec{u} + \left(\nabla \vec{u} \right)^T \right) - \frac{2}{3} \mu \left(\nabla \cdot \vec{u} \right) \vec{I} \right\} \right] - \left(\kappa^{-1} \mu + \frac{Q_m}{\varepsilon_p^2} \right) \vec{u} + \vec{F} \quad (10)$$

where ε_p indicates a porosity [-], $\vec{I}$ indicates an unit vector [-], and $\vec{F}$ indicates a force vector [kg/(m³·s)].

The equation of mass transfer in porous material can be defined by the Maxwell-Stefan equation, as following:

$$\nabla \cdot \left(\rho \omega_i \vec{u} - \rho \omega_i \sum_{k=1}^n \varepsilon_p^{\frac{3}{2}} \tilde{D}_{ik} \left(\nabla x_k + (x_k - \omega_k) \frac{\nabla p}{p} \right) - \varepsilon_p^{\frac{3}{2}} D_i^T \frac{\nabla T}{T} \right) = R_{i,tot} \quad (11)$$

where ω_i , ω_k indicates a mass ratio of chemicals i and k , respectively [-], $\tilde{D}_{ik}$ indicates a Fick's diffusion coefficient of effective multi components [m²/s], D_i^T indicates a thermal diffusion coefficient [kg/(m·s)], and $R_{i,tot}$ indicates a reaction rate of chemical species [mol/(m³·s)].

The equations of heat transfer in porous material can be defined as following:

$$\rho_f C_{p,f} \vec{u} \cdot \nabla T + \nabla \cdot \vec{q} = Q + Q_p + Q_{vd} \quad (12)$$

$$\vec{q} = -k_{eff} \nabla T \quad (13)$$

where f indicates a physical quantity on fluid [-], C_p indicates a constant pressure specific heat [J/(kg·K)], $\vec{q}$ indicates a thermal flux vector [W/m²], Q indicates a thermal source [W/m³], Q_p indicates a thermal source due to pressure loss [W/m³], Q_{vd} indicates a thermal source due to viscosity dissipation [W/m³], and k_{eff} indicates an effective thermal conductivity [W/(m·K)].

Since there are more previous studies using COMSOL Multiphysics for numerical analysis on BDR and reports the reaction characteristics as well as heat and mass transfer [18–21], we have adopted COMSOL Multiphysics for the numerical analysis in this study.

2.2. 2D Numerical Simulation Model of BDR Membrane Reactor

Figure 1 illustrates the overview of 2D model. The dimension of reaction chamber and sweep chamber in 2D model is 40 mm × 100 mm. The inlet and the outlet of reaction chamber and sweep chamber are set in 2D model. The length of inlet and outlet of reaction chamber and sweep chamber is 6 mm, which is located vertically in Figure 1. Pd/Cu membrane which is used for H₂ separation is located between the reaction chamber and the sweep chamber. The thickness of Pd/Cu membrane is 20 μm, 40 μm and 60 μm, which is followed from the authors' previous experimental studies [23,24].

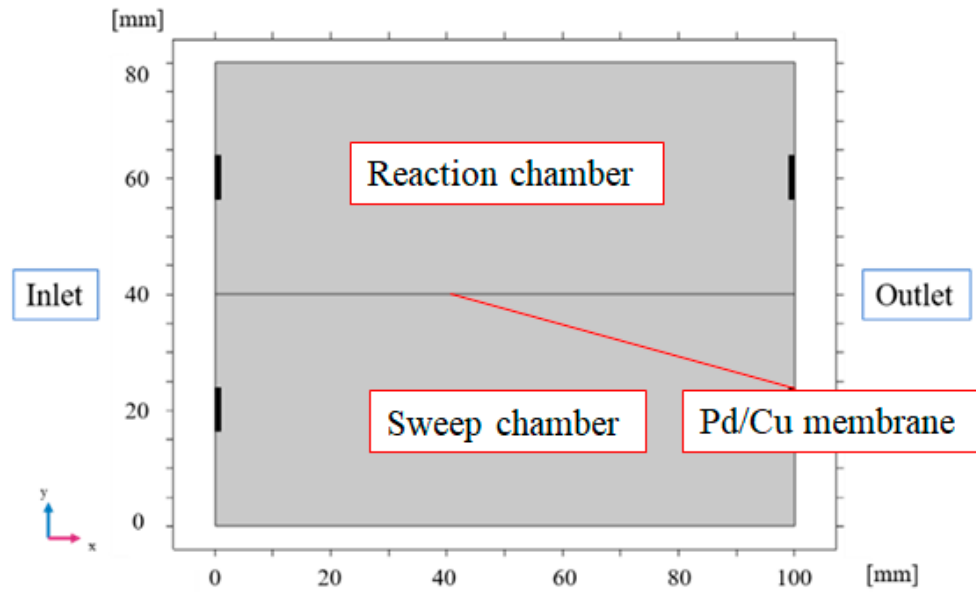


Figure 1. Schematic drawing of 2D model used for numerical simulation in this study.

2.3. Kinetic Modeling of BDR

This study considers the reaction scheme shown by Equations (1) – (6) for the numerical simulation. Reaction rates of these equations are defined as follows [25–27]:

<Dry reforming (DR)>

$$r_1 = k_1 \cdot \left[\frac{K_{CO_2,1} K_{CH_4,1} P_{CO_2} P_{CH_4}}{(1 + K_{CO_2,1} P_{CO_2} + K_{CH_4,1} P_{CH_4})^2} \right] \cdot \left[1 - \frac{(P_{CO} P_{H_2})^2}{K_1 P_{CO_2} P_{CH_4}} \right] \quad (14)$$

where $k_1 = 1290 \times 5000 e^{\frac{-102065}{RT}}$, $K_{CO_2,1} = 2.64 \times 10^{-2} e^{\frac{37641}{RT}}$, $K_{CH_4,1} = 2.63 \times 10^{-2} e^{\frac{40684}{RT}}$,
 $K_1 = e^{34.011} \cdot e^{\frac{-258598}{RT}}$.

<Reverse water gas shift reaction (RWGS)>

$$r_2 = k_2 P_{CO_2} \left(1 - \frac{P_{CO} P_{H_2O}}{K_2 P_{CO_2} P_{H_2}} \right) \quad (15)$$

where $k_2 = 9.28 \times 10^3 e^{\frac{-73105}{RT}}$, $K_2 = 68.78 e^{\frac{-37500}{RT}}$.

<Steam reforming (SR)>

$$r_3 = \frac{\frac{k_3}{P_{H_2}^{2.5}} \left(P_{CH_4} P_{H_2O} - \frac{P_{CO} P_{H_2}^3}{K_3} \right)}{\left(1 + \frac{P_{H_2O} K_{H_2O,2}}{P_{H_2}} + K_{CO,2} P_{CO} + K_{H_2,2} P_{H_2} + K_{CH_4,2} P_{CH_4} \right)^2} \quad (16)$$

where $k_2 = 2.636 \times 10^{12} e^{\frac{-240100}{RT}}$, $K_2 = 1.198 \times 10^{17} e^{\frac{-26830}{RT}}$, $K_{CO_2,2} = 8.23 \times 10^{-5} e^{\frac{70650}{RT}}$,
 $K_{CH_4,2} = 6.65 \times 10^4 e^{\frac{38280}{RT}}$, $K_{H_2,2} = 6.12 \times 10^{-9} e^{\frac{82900}{RT}}$, $K_{H_2O,2} = 1.77 \times 10^5 e^{\frac{-88680}{RT}}$.

<Methanation reaction (MR)>

$$r_4 = \frac{\frac{k_4}{P_{H_2}^{3.5}} \left(P_{CH_4} P_{H_2O}^2 - \frac{P_{CO_2} P_{H_2}^4}{K_4} \right)}{\left(1 + \frac{P_{H_2O} K_{H_2O,4}}{P_{H_2}} + K_{CO,4} P_{CO} + K_{H_2,4} P_{H_2} + K_{CH_4,4} P_{CH_4} \right)^2} \quad (17)$$

where $k_4 = 6.364 \times 10^{11} e^{\frac{-24390}{RT}}$, $K_4 = 2.117 \times 10^{15} e^{\frac{-22430}{RT}}$, $K_{CH_4,4} = 6.65 \times 10^{-4} e^{\frac{38280}{RT}}$,
 $K_{CO,4} = 8.23 \times 10^{-5} e^{\frac{70650}{RT}}$, $K_{H_2,4} = 6.12 \times 10^{-9} e^{\frac{82900}{RT}}$, $K_{H_2O,4} = 1.77 \times 10^5 e^{\frac{-88680}{RT}}$.

<Methane decomposition reaction (MDR)>

$$r_5 = \frac{k_5 K_{CH_4,5} \left(P_{CH_4} - \frac{P_{H_2}^2}{K_5} \right)}{\left(1 + K_{CH_4,5} P_{CH_4} + \frac{P_{H_2}^{1.5}}{K_{H_2,5}} \right)^2} \quad (18)$$

where $k_5 = 6.95 \times 10^3 e^{\frac{-58983}{RT}}$, $K_5 = 2.95 \times 10^5 e^{\frac{-84440}{RT}}$, $K_{CH_4,5} = 0.21 e^{\frac{-567}{RT}}$, $K_{H_2,5} = 5.18 \times 10^7 e^{\frac{-133210}{RT}}$.

<Boudouard reaction (BD)>

$$r_6 = \frac{\frac{k_6}{K_{CO,6} K_{CO_2,6}} \left(\frac{P_{CO}}{K_6} - \frac{P_{CO_2}}{P_{CO}} \right)}{\left(1 + K_{CO,6} P_{CO} + \frac{1}{K_{CO,6} K_{CO_2,6}} \frac{P_{CO_2}}{P_{CO}} \right)^2} \quad (19)$$

where $k_6 = 1.34 \times 10^{15} e^{\frac{-243835}{RT}}$, $K_6 = 1.9393 \times 10^9 e^{\frac{-168527}{RT}}$, $K_{CO_2,6} = 2.81 \times 10^7 e^{\frac{-104085}{RT}}$,
 $K_{CO,6} = 7.34 \times 10^{-6} e^{\frac{100395}{RT}}$. In addition, r_n is a kinetic rate ($n = 1, 2, 3, 4, 5, 6$) [mol/(kg · s)], k_n is a kinetic constant ($n = 1, 2, 3, 4, 5, 6$) [mol/(kg · s)], P_i is a particle pressure of chemical species i [Pa], K_n is an equilibrium constant ($n = 1, 2, 3, 4, 5, 6$) [-] and K_i is an absorption equilibrium constants of chemical species i [-].

2.4. Numerical Simulation Parameters and Conditions in This Study

In this study, the molar ratio of CH₄:CO₂ is set at 1.5:1, which simulates a biogas. The initial reaction temperature is changed by 400 °C, 500 °C and 600 °C. Ni/Cr alloy is assumed to be the catalyst, which was used for the authors' previous experimental studies [5,24]. The weight ratio of Cr to the whole weight of Ni/Cr alloy is 20 wt%. The porosity, permeability, constant pressure specific heat and thermal conductivity of Ni/Cr alloy catalysts are estimated considering the weight ratio of Cr. The porosity (ε_p) is set at 0.95.

The thickness of Pd/Cu membrane is changed by 20 μm, 40 μm and 60 μm. Table 1 lists the main physical properties and parameters for the numerical simulation in this study.

Table 1. Numerical simulation conditions adopted in this study.

Initial reaction temperature [°C]	400, 500, 600
Pressure in reactor [Pa]	1.013×10^5
Inlet flow rate of CH ₄ [NL/min]	1.088

(CH ₄ :CO ₂ = 1.5:1)	
Inlet flow rate of CO ₂ [NL/min]	0.725
(CH ₄ :CO ₂ = 1.5:1)	
Outlet pressure [Pa]	1.013×10^5
Density of catalyst [kg/m ³]	1045, 1042, 1040 (@400 °C, 500 °C, 600 °C)
Porosity of catalyst (ϵ_p) [-]	0.95
Permeability of catalyst [m ²]	1.7×10^{-8} , 1.6×10^{-8} , 1.5×10^{-9}
Constant pressure of specific heat of catalyst [J/(kg·K)]	327, 333, 340
Thermal conductivity of catalyst [W/(m·K)]	197, 194, 192

In this study, the following assumptions are set:

- (i) Catalyst is a porous material. The porosity, permeability, constant pressure specific heat and thermal conductivity and isotropic.
- (ii) Wall temperature is isothermal.
- (iii) Gas is a Newton fluid and an ideal gas.
- (iv) Wall of reactor excluding inlet and outlet is no-slip.
- (v) The pressure of outlet is atmosphere (gauge pressure = 0 Pa).
- (vi) The temperature of inflow gas is same as the initial reaction temperature.
- (vii) The produced carbon is treated as a gas.

As to (vii), a solid carbon is produced by Equations (5) and (6) generally. However, COMSOL Multiphysics used by this study can't treat a solid carbon and treat a gaseous carbon. Consequently, this study has considered the assumption (vii).

2.5. Evaluation Factor for Reaction Characteristics in This Study

In this study, the evaluation factors are considered as follows:

$$\text{CH}_4 \text{ conversion} = \frac{C_{\text{CH}_4, \text{in}} - C_{\text{CH}_4, \text{out}}}{C_{\text{CH}_4, \text{in}}} \times 100 \quad [\%] \quad (20)$$

where $C_{\text{CH}_4, \text{in}}$ means a molar concentration of CH₄ at the inlet [mol], $C_{\text{CH}_4, \text{out}}$ means a molar concentration of CH₄ at the outlet [mol].

$$\text{CO}_2 \text{ conversion} = \frac{C_{\text{CO}_2, \text{in}} - C_{\text{CO}_2, \text{out}}}{C_{\text{CO}_2, \text{in}}} \times 100 \quad [\%] \quad (21)$$

where $C_{\text{CO}_2, \text{in}}$ means a molar concentration of CO₂ at the inlet [mol], $C_{\text{CO}_2, \text{out}}$ means a molar concentration of CO₂ at the outlet [mol].

$$\text{H}_2 \text{ yield} = \frac{\frac{1}{2} C_{\text{H}_2, \text{out}}}{C_{\text{CH}_4, \text{in}}} \times 100 \quad [\%] \quad (22)$$

where $C_{\text{H}_2, \text{out}}$ means a molar concentration of H₂ at the outlet [mol].

$$\text{H}_2 \text{ selectivity} = \frac{C_{\text{H}_2, \text{out}}}{C_{\text{H}_2, \text{out}} + C_{\text{CO}, \text{out}}} \times 100 \quad (23)$$

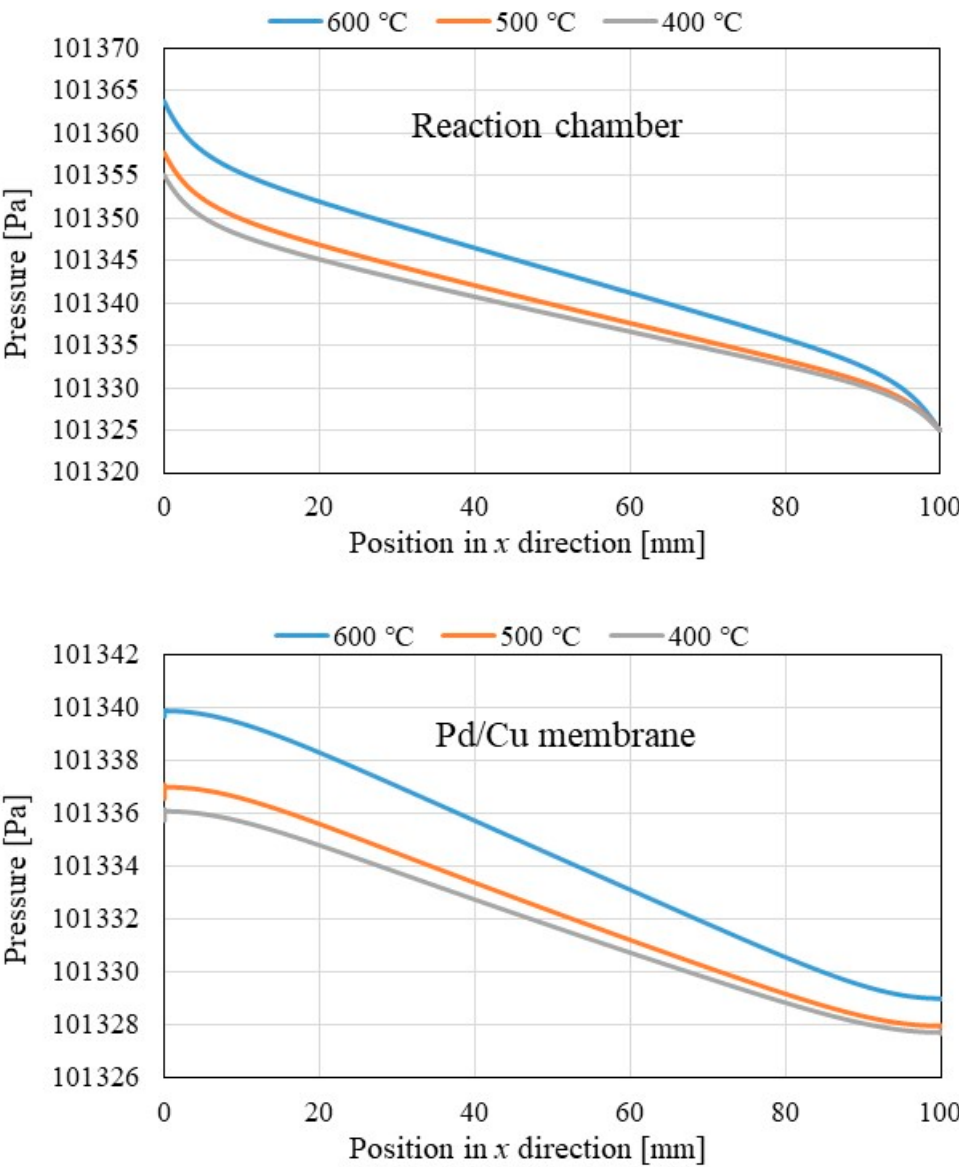
where $C_{\text{CO}, \text{out}}$ means a molar concentration of CO at the outlet [mol].

$$\text{CO selectivity} = \frac{C_{\text{CO}, \text{out}}}{C_{\text{H}_2, \text{out}} + C_{\text{CO}, \text{out}}} \times 100 \quad [\%] \quad (24)$$

3. Results and Discussion

3.1. Comparison of the Distriburtion of Pressure along x Direction among Different Initial Reaction Temperature and Thickness of Pd/Cu Membrane

Figure 2 shows the comparison of the distribution of pressure along x direction in reaction chamber ($y = 62$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm) changing the initial reaction temperature. In this figure, the thickness of Pd/Cu membrane is $20\text{ }\mu\text{m}$.



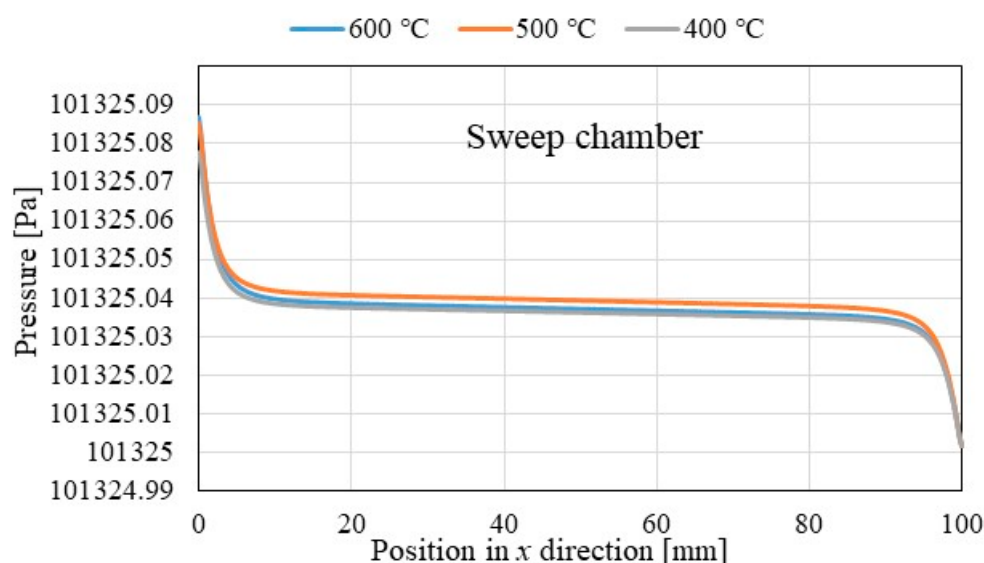


Figure 2. Impact of the initial reaction temperature on the distribution of pressure along x direction in reaction chamber ($y = 62$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm).

It is seen from Figure 2 that the pressure in reaction chamber as well as Pd/Cu membrane decreases along x direction. This is due to the permeation resistance of porous catalyst and Pd/Cu membrane. In addition, we can know that the pressure in reaction chamber as well as Pd/Cu membrane increases with the increase in the initial reaction temperature. It is thought from the state equation, i.e. $pV = nRT$ that the pressure increases with the increase in the temperature. Moreover, the pressures near the inlet and the outlet changes rapidly, especially for those in sweep chamber. Since the length of inlet and outlet of reaction chamber and sweep chamber is 6 mm which is shorter than the height of reaction chamber and sweep chamber of 40 mm, the large pressure change occurs due to the change in cross sectional area for the gas flow.

Figure 3 shows the comparison of the distribution of pressure along x direction in reaction chamber ($y = 62$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm) changing the thickness of Pd/Cu membrane. In this figure, the initial reaction temperature is 600 °C. It is seen from Figure 3 that the pressure in reaction chamber as well as Pd/Cu membrane decreases along x direction. This is due to the permeation resistance of porous catalyst and Pd/Cu membrane. According to Figure 3, the pressure in Pd/Cu membrane is higher with the decrease in the thickness of Pd/Cu membrane though the impact of the thickness of Pd/Cu membrane on pressure in reaction chamber and sweep chamber is very small. Since the permeation resistance decreases with the decrease in the thickness of Pd/Cu membrane, the pressure in Pd/Cu membrane is higher.

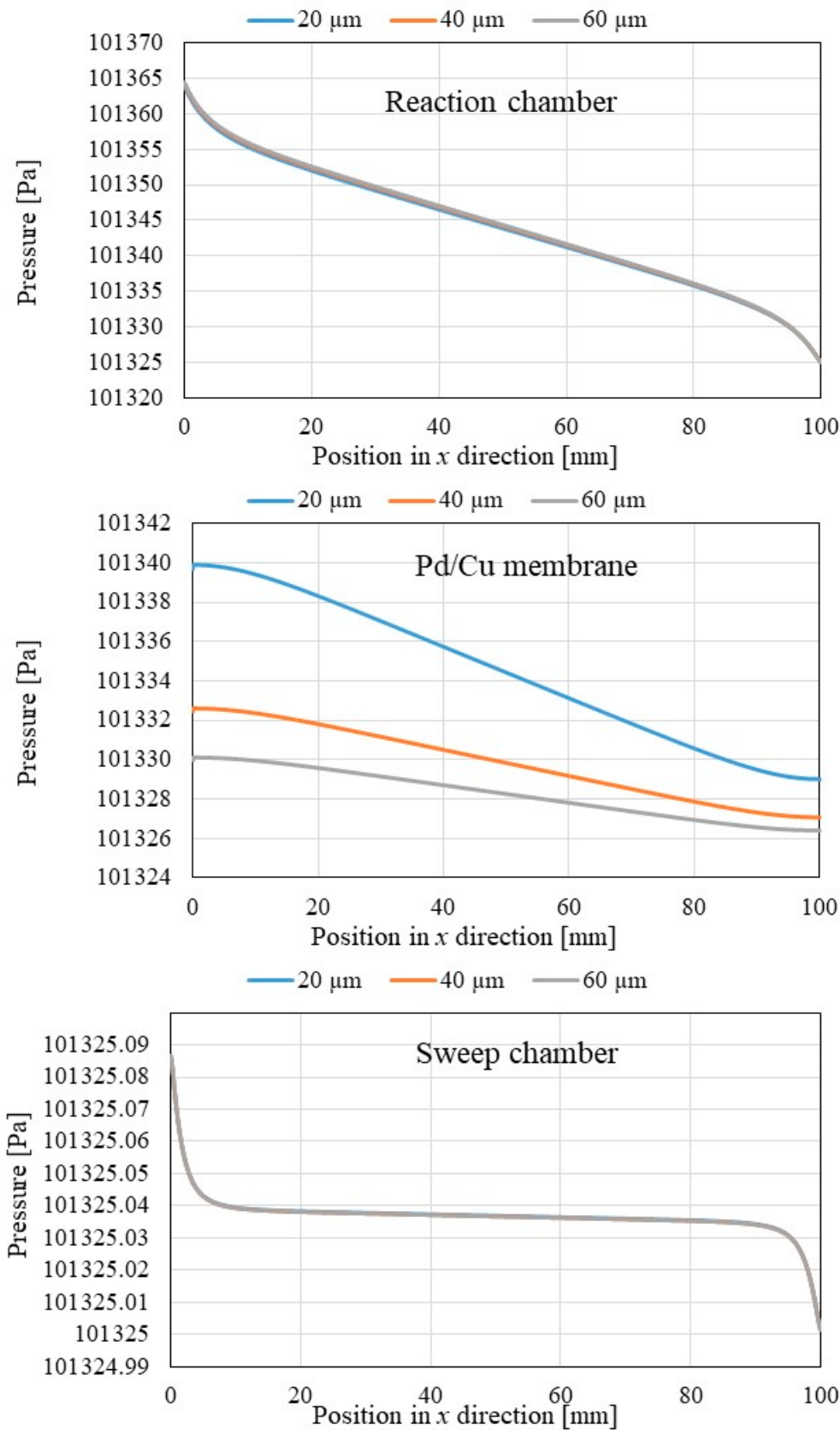


Figure 3. Impact of the thickness of Pd/Cu membrane on the distribution of pressure along x direction in reaction chamber ($y = 62$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm).

3.2. Comparison of Each Gas Concentration along x Direction among Different Initial Reaction Temperature and Thickness of Pd/Cu Membrane

Figure 4 shows the comparison of distribution of each gas concentration along x direction in reaction chamber ($y = 62$ mm) among different initial reaction temperatures. The thickness of Pd/Cu membrane is $20\text{ }\mu\text{m}$ in this figure. According to Figure 4, it is clear that the molar concentrations of CH_4 and CO_2 decrease with the increase in the initial reaction temperature, while the molar concentrations of H_2 , CO , H_2O and C increase with the increase in the initial reaction temperature. Since Equation (1) is an endothermic reaction, it can be thought the molar concentrations of CH_4 and CO_2 decrease and those of H_2 and CO increase with the increase in the initial reaction temperature. As to the formation of H_2O and C , it is thought that Equations (3), (4), (5) and (6) might occur. The formation of H_2O and C were observed by the authors' previous experimental study [23]. After the experiments, carbon was observed as shown in Figure 5 [23]. On the other hand, the formation of H_2O was confirmed by the observation by means of the gas bag shown in Figure 6.

Figure 7 shows the impact of the initial reaction temperature on distributions of molar concentration of H_2 along x direction in reaction chamber ($y = 62$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm). It is seen from Figure 7 that the molar concentration of H_2 increases along through x direction in reaction chamber, Pd/Cu membrane and sweep chamber. Since the H_2 production reactions, i.e., Equations (1), (2) and (5) occur along through x direction, the molar concentration of H_2 increases along through x direction. In addition, it is observed that the molar concentration of H_2 in reaction chamber, Pd/Cu membrane and sweep chamber increases with the increase in the initial reaction temperature. Since the H_2 production reactions, i.e., Equations (1), (2) and (5) are endothermic reactions, the molar concentration of H_2 increases with the increase in the initial reaction temperature. In addition, it is known from Figure 7 that the molar concentrations of H_2 in Pd/Cu membrane and sweep chamber are higher when the molar concentration of H_2 in reaction chamber is higher. Since the molar concentration of H_2 in reaction chamber is higher, the driving force to permeate the Pd/Cu membrane being stronger due to the large H_2 partial pressure difference between the reaction chamber and the sweep chamber [23]. As a result, the molar concentration of H_2 in Pd/Cu membrane and sweep chamber are higher.

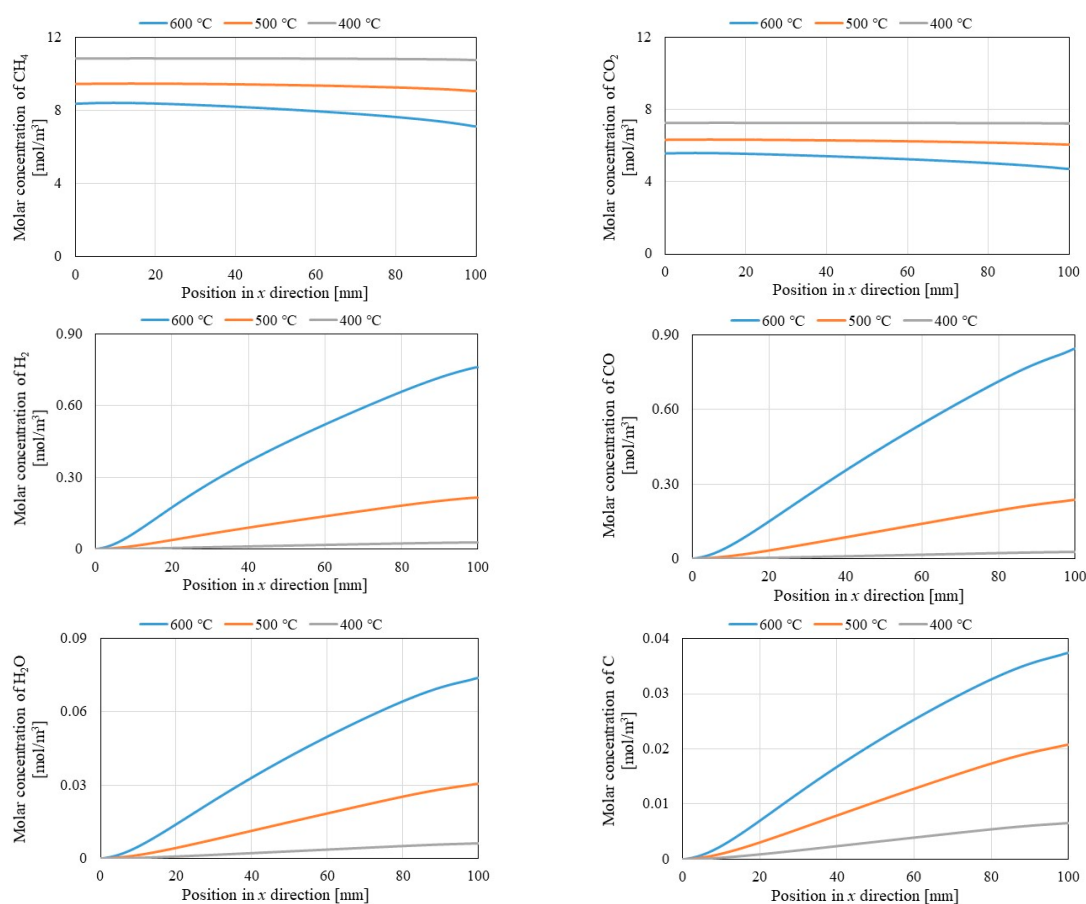


Figure 4. Impact of the initial reaction temperature on the distribution of each gas concentration along x direction in reaction chamber ($y = 62$ mm).

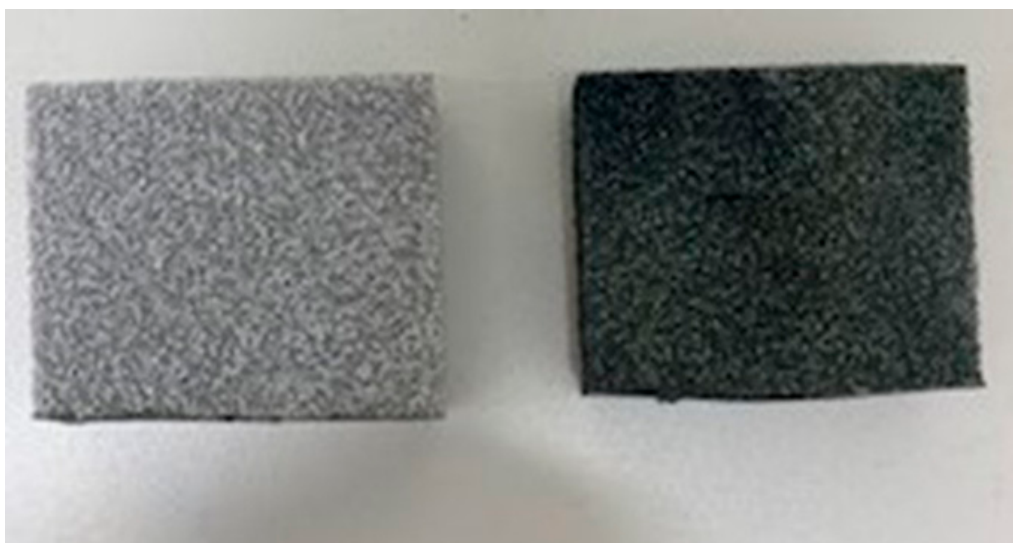


Figure 5. Photo of Ni/Cr catalyst before and after experiments (left: before experiment, right: after experiment) [23].



Figure 6. Photo of produced H_2O observed using gas bag [23].

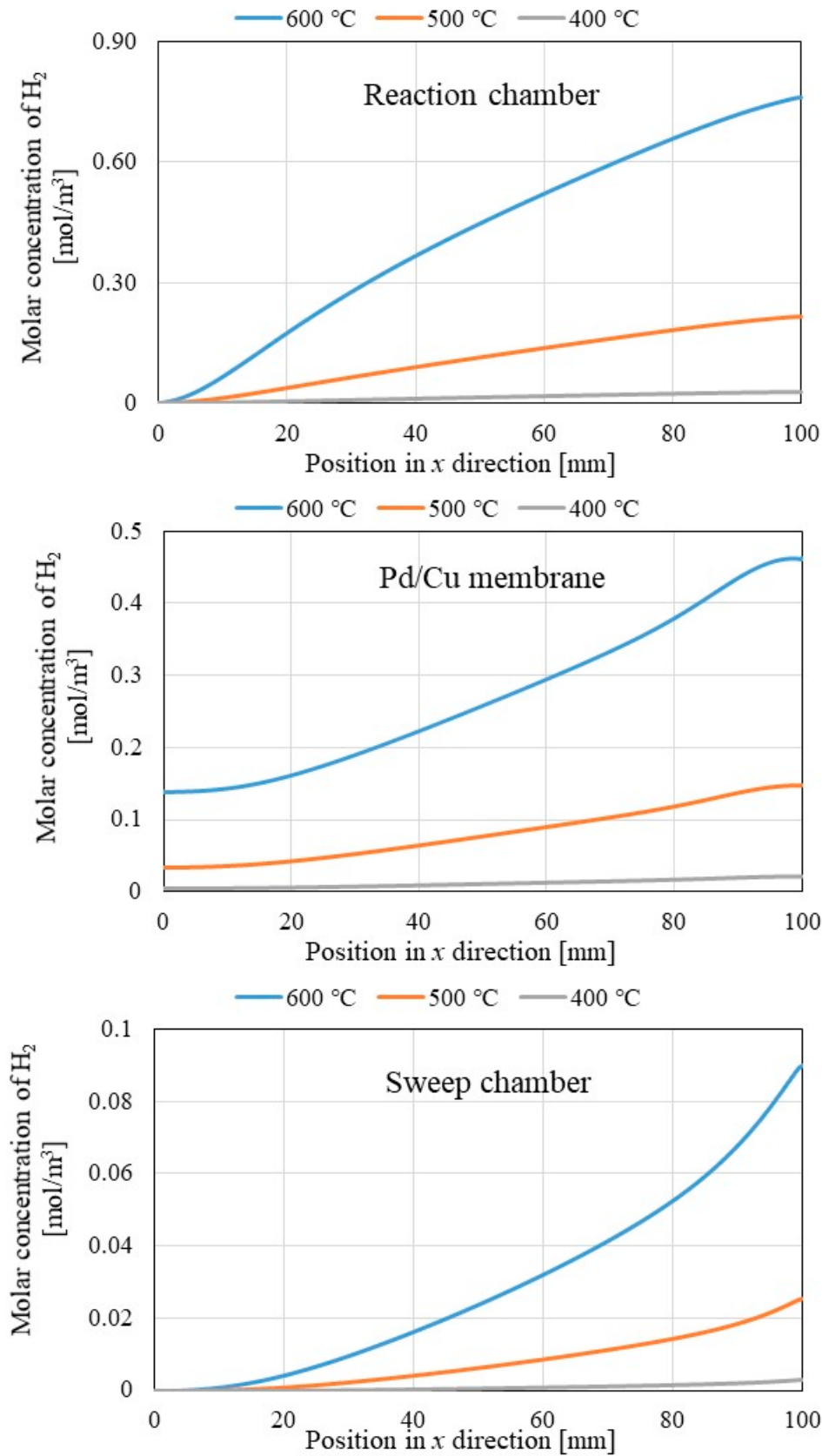


Figure 7. Impact of the initial reaction temperature on distribution of molar concentration of H_2 along x direction in reaction chamber ($y = 60$ mm), Pd/Cu membrane ($y = 40$ mm) and sweep chamber ($y = 20$ mm).

Figure 8 shows the comparison of distribution of each gas concentration along x direction in reaction chamber ($y = 62$ mm) among different thicknesses of Pd/Cu membrane. It is seen from Figure 8 that the impact of thickness of Pd/Cu membrane on each gas concentration along x direction in

reaction chamber is small. However, it is found that the molar concentrations of H_2 in Pd/Cu membrane and sweep chamber increase with the decrease in the thickness of Pd/Cu membrane according to Figure 9. Since the penetration resistance of Pd/Cu membrane decreases with the decrease in the thickness of Pd/Cu membrane, the molar concentrations of H_2 in Pd/Cu membrane and sweep are higher with the decrease in the thickness of Pd/Cu membrane.

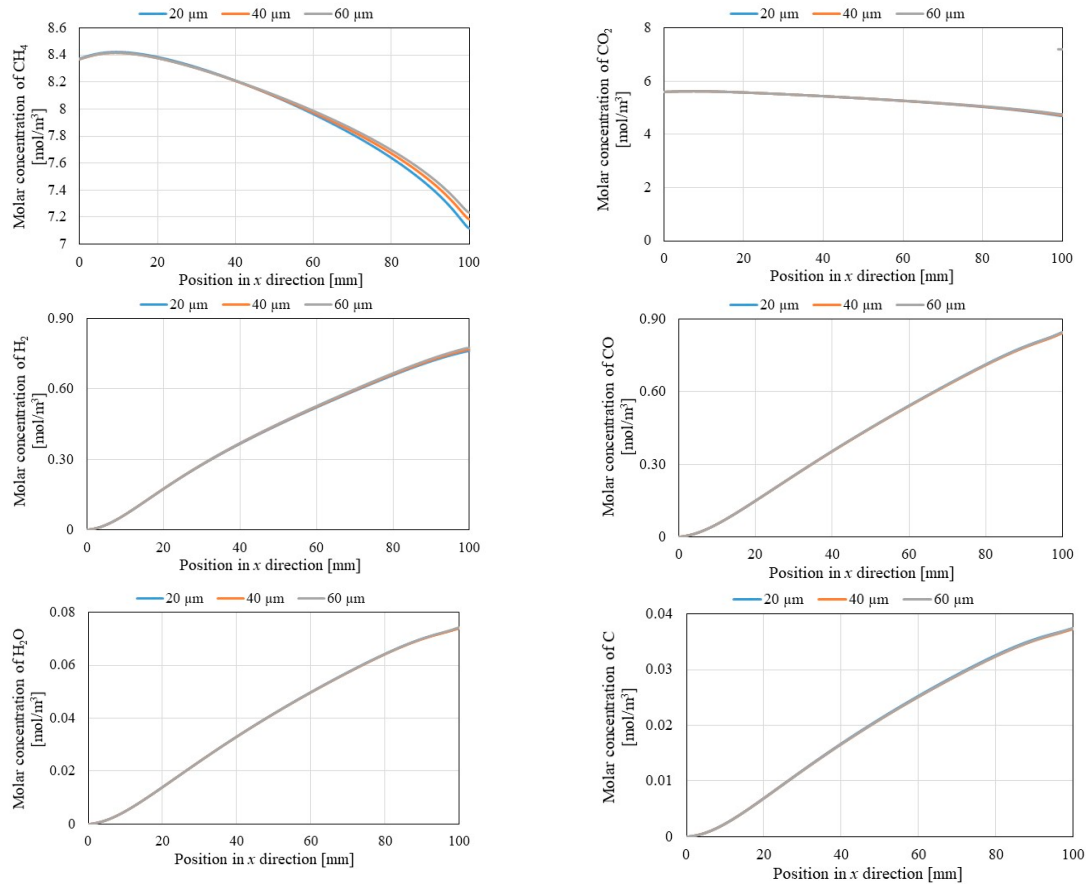
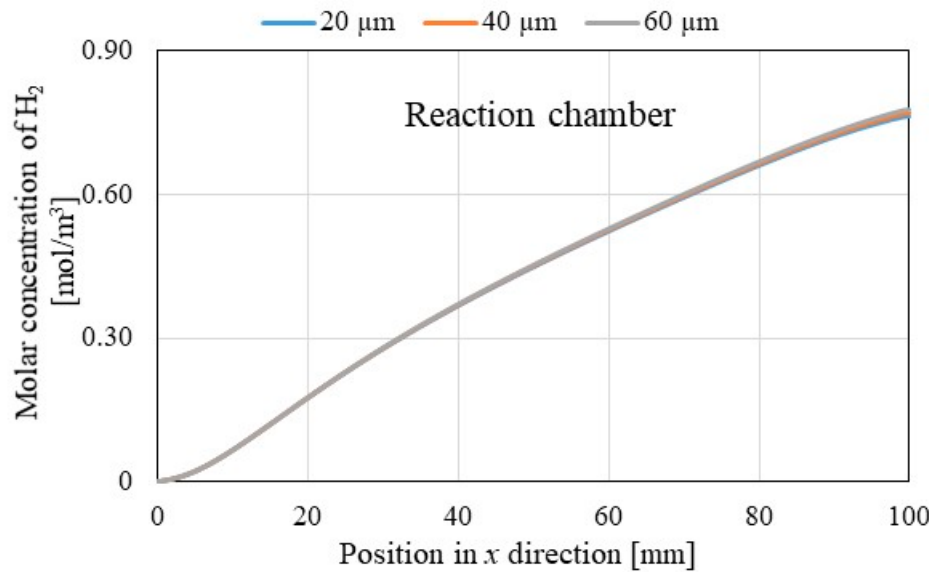


Figure 8. Impact of the thickness of Pd/Cu membrane on the distribution of each gas concentration along x direction in reaction chamber ($y = 62$ mm).



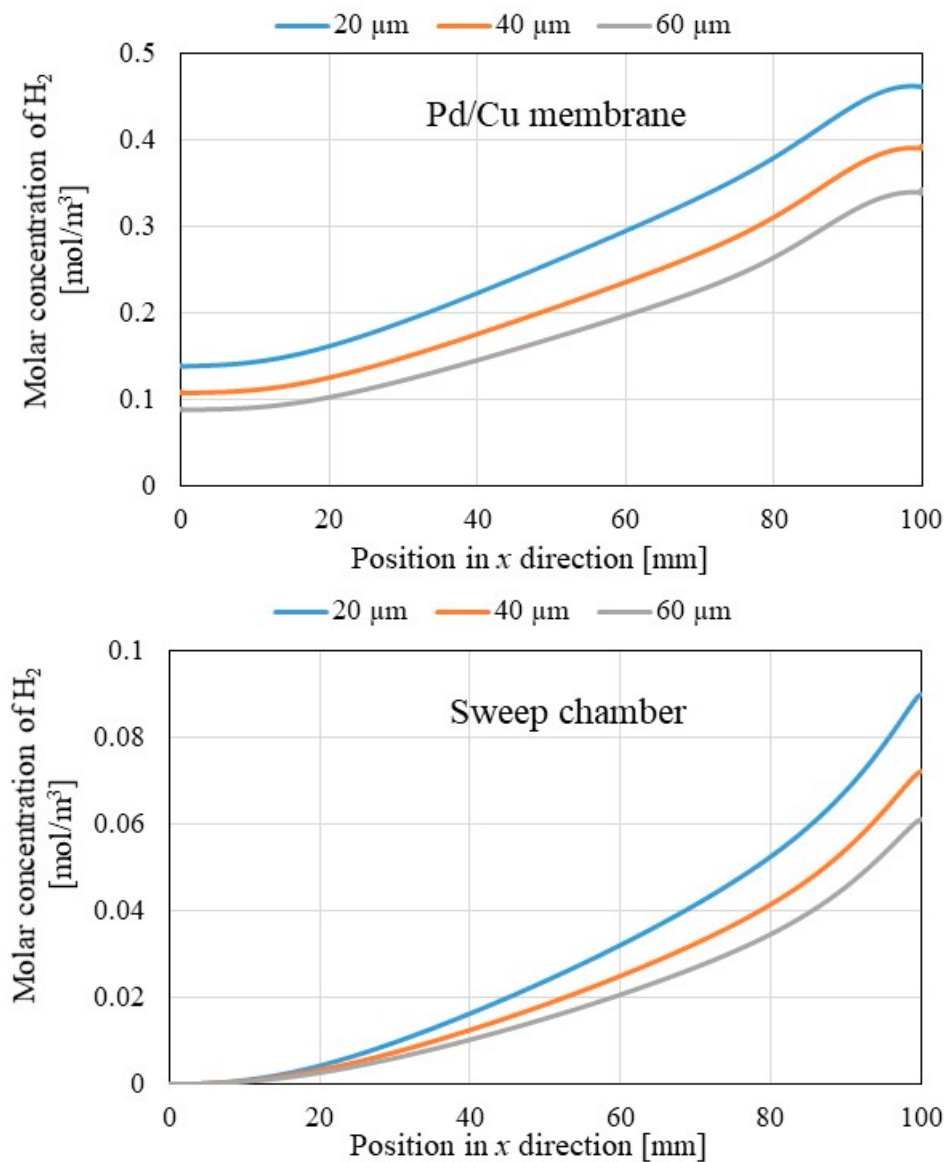


Figure 9. Impact of the thickness of Pd/Cu membrane on distribution of molar concentration of H₂ along *x* direction in reaction chamber (*y* = 60 mm), Pd/Cu membrane (*y* = 40 mm) and sweep chamber (*y* = 20 mm).

3.3. Investigation on Reaction Characteristics by Evaluation Factors

To investigate the reaction characteristics of BDR including the other reactions considered in this study, Table 2 lists CH₄ conversion, CO₂ conversion, H₂ yield, H₂ selectivity and CO selectivity for various initial temperature using the thickness of Pd/Cu membrane of 20 μm and various thickness of Pd/Cu membrane at the initial temperature of 600 °C.

Table 2. Comparison of CH₄ conversion, CO₂ conversion, H₂ yield, H₂ selectivity and CO selectivity for various initial temperature using the thickness of Pd/Cu membrane of 20 μm and various thickness of Pd/Cu membrane at the initial temperature of 600 °C.

Initial reaction temperature [°C]	Thickness of Pd/Cu membrane of 20 μm				
	CH ₄ conversion [%]	CO ₂ conversion [%]	H ₂ yield [%]	H ₂ selectivity [%]	CO selectivity [%]
600	15.0	15.9	5.09	49.1	50.9
500	4.03	3.73	1.14	46.4	53.6

400	1.10	0.49	0.15	52.2	47.8
Initial temperature of 600 °C					
Thickness of Pd/Cu membrane [m]	CH ₄ conversion [%]	CO ₂ conversion [%]	H ₂ yield [%]	H ₂ selectivity [%]	CO selectivity [%]
20	15.0	15.9	5.09	49.1	50.9
40	14.2	15.4	5.02	49.2	50.8
60	13.5	15.0	5.00	49.2	50.8

According to Table 2, it is revealed that CH₄ conversion, CO₂ conversion and H₂ yield increase with the increase in the initial reaction temperature. Since Equations (1), (2), (3) and (5) are endothermic reactions, the consumption of CH₄ and CO₂ as well as the production of H₂ increase more with the increase in the initial reaction temperature. In addition, it is clear from Table 2 that CH₄ conversion, CO₂ conversion and H₂ yield increase with the decrease in the thickness of Pd/Cu membrane. Since the penetration resistance of Pd/Cu membrane decreases with the decrease in the thickness of Pd/Cu membrane, the permeation of H₂ through Pd/Cu membrane is promoted. As a result, it is thought that Equations (1), (2) and (5), which are reactions of producing H₂, would be non-equilibrium state. Therefore, the consumption of CH₄ and CO₂ as well as the production of H₂ increase more with the decrease in the thickness of Pd/Cu membrane. According to Equation (5), C would be produced more if the reaction becomes non-equilibrium state by separating H₂ from reaction chamber via Pd/Cu membrane. This phenomenon is confirmed by Figure 4.

As described in Introduction part, the previous studies reported that CH₄ conversion and CO₂ conversion are approximately 40 - 100 % and 50 - 100 %, respectively [7–14]. These values of CH₄ conversion and CO₂ conversion are higher than those obtained in this study. This study thinks that the initial reaction temperature of 600 °C is not enough to obtain higher performance of BDR, which is compared to the previous studies [7–14]. According to the previous reports using Ni alloy catalysts, CH₄ conversion, H₂ yield and H₂ selectivity increased with the increase in the initial reaction temperature and higher values were obtained over 600 °C [28–31]. This study proposes that the following subjects can be considered to improve the performance of H₂ production: (i) the optimization of catalyst shape and composition, (ii) the optimization of thickness and composition of Pd/Cu membrane, (iii) the optimization of H₂ separation rate of Pd/Cu membrane and H₂ production rate of the catalyst. This study would like to conduct these subjects.

4. Conclusions

This study has clarified the characteristics of BDR in the membrane reactor using Pd/Cu membrane and Ni/Cr catalyst by the numerical simulation with COMSOL Multiphysics. The initial reaction temperature has been changed by 400 °C, 500 °C and 600 °C. The thickness of Pd/Cu membrane has been changed by 20 µm, 40 µm and 60 µm. As a result, the following conclusions can be drawn:

- The pressure in reaction chamber as well as Pd/Cu membrane decreases along x direction and they increase with the increase in the initial reaction.
- The pressure in Pd/Cu membrane is higher with the decrease in the thickness of Pd/Cu membrane though the impact of the thickness of Pd/Cu membrane on pressure in reaction chamber and sweep chamber is very small.
- It is revealed that the molar concentrations of CH₄ and CO₂ decrease with the increase in the initial reaction temperature, while the molar concentrations of H₂, CO, H₂O and C increase with the increase in the initial reaction temperature. Since Equation (1) is an endothermic reaction, the molar concentrations of CH₄ and CO₂ decrease and those of H₂ and CO increase with the increase in the initial reaction temperature. In addition, H₂O and C are formed since it is thought that Equations (3), (4), (5) and (6) occur.

- (iv) It is revealed that the molar concentration of H₂ increases along through x direction in reaction chamber, Pd/Cu membrane and sweep chamber. Since the H₂ production reactions, i.e., Equations (1), (2) and (5) occur along through x direction, the molar concentration of H₂ increases along through x direction.
- (v) It is revealed that the molar concentrations of H₂ in reaction chamber, Pd/Cu membrane and sweep chamber increase with the increase in the initial reaction temperature. Since the H₂ production reactions, i.e., Equations (1), (2) and (5) are endothermic reactions, the molar concentration of H₂ increases with the increase in the initial reaction temperature.
- (vi) The molar concentrations of H₂ in Pd/Cu membrane and sweep chamber are higher when the molar concentration of H₂ in reaction chamber is higher. Since the molar concentration of H₂ in reaction chamber is higher, the driving force to permeate the Pd/Cu membrane is stronger due to the large H₂ partial pressure difference between the reaction chamber and the sweep chamber.
- (vii) It is revealed that the molar concentrations of H₂ in Pd/Cu membrane and sweep chamber increase with the decrease in the thickness of Pd/Cu membrane. Since the penetration resistance of Pd/Cu membrane decreases with the decrease in the thickness of Pd/Cu membrane, the molar concentrations of H₂ in Pd/Cu membrane and sweep are higher with the decrease in the thickness of Pd/Cu membrane.
- (viii) It is revealed that CH₄ conversion, CO₂ conversion and H₂ yield increase with the increase in the initial reaction temperature as well as the decrease in the thickness of Pd/Cu membrane.

Author Contributions: Conceptualization and writing—original draft preparation, A.N.; methodology and software, R.I. and S.Y.; data curation, M.I. and T.H.; writing—review and editing, E.H..

Funding: This research was funded by KRI cooperation.

Data Availability Statement: The authors agree to share the data of the article published in this journal.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Kalai, D.Y.; Stangeland, K.; Jin, R.; Tucho, W.M.; Yu, Z. Biogas dry reforming for syngas production on La promoted hydrotalcite-derived Ni Catalyst. *Int. J. Hydrogen Energy* **2018**, *43*, 19438-19450.
- World Bioenergy Association. Available online: <https://worldbioenergy.org/global-bioenergy-statistics> (accessed on 12 December 2024).
- The Japan Gas Association. Available online: <https://www.gas.or.jp/gas-life/biogas/> (accessed on 12 December 2024).
- Nishimura, A.; Takada, T.; Ohata, S.; Kolhe, M.L. Biogas dry reforming for hydrogen through membrane reactor utilizing negative pressure. *Fuels* **2021**, *2*, 194-209.
- Nishimura, A.; Hayashi, Y.; Ito, S.; Kolhe, M.L. Performance analysis of hydrogen production for a solid oxide fuel cell system using a biogas dry reforming membrane reactor with Ni and Ni/Cr catalysts. *Fuels* **2023**, *4*, 295-313.
- Nishimura, A.; Sato, R.; Hu, E. An energy production system powered by solar heat with biogas dry reforming reactor and solar heat with biogas dry reforming reactor and solid oxide fuel cell. *Smart Grid and Renew. Energy* **2023**, *14*, 85-106.
- Dogan, M. Y.; Arbag, H.; Tasdemir, M.; Yasyerli, N.; Yasyerli, S. Effect of ceria content in Ni-Ce-Al catalyst on catalytic performance and carbon/coke formation in dry reforming of CH₄. *International Journal of Hydrogen Energy* **2023**, *48*, 23013-23030.
- Kiani, P.; Meshksar, M.; Rahimpour, M. R. Biogas reforming over La-promoted Ni/SBA-16 catalyst for syngas production: catalytic structure and process activity investigation. *International Journal of Hydrogen Energy* **2023**, *48*, 6262-6274.
- Carrasco-Ruiz, S.; Zhang, Q.; Gandara-Loe, J.; Pastor-Perez, L.; Odriozola, J. A.; Reina, T. R.; Bobadilla, L. F. H₂-rich syngas production from biogas reforming: overcoming coking and sintering using bimetallic Ni-based catalysts. *International Journal of Hydrogen Energy* **2023**, *48*, 27907-27917.
- Ponugoti, P. V.; Pathmanathan, P.; Rapolu, J.; Gomathi, A.; Janardhanan, V. M. On the stability of Ni/ γ -Al₂O₃ catalyst and the effect of H₂O and O₂ during biogas reforming. *Applied Catalysis A, General* **2023**, *651*, doi:10.1016/j.apcata.2023.119033.
- Martin-Espejo, J. L.; Merkouri, L. P.; Gandara-Loe, J.; Odriozola, J. A.; Reina, T. R.; Pastor-Perez, L. Nickel-based cerium zirconate inorganic complex structures for CO₂ valorisation via dry reforming of methane. *Journal of Environmental Sciences* **2024**, *140*, 12-23.

12. Cao, A. N. T.; Nguyen, H. H.; Pham, T. P. T.; Pham, L. K. H.; Phuong, D. H. L.; Nguyen, N. A.; Vo, D. V. N.; Pham, P. T. H. Insight into the role of material basicity in the coke formation and performance of Ni/Al₂O₃ catalyst for the simulated-biogas dry reforming. *Journal of the Energy Institute* **2023**, 108, doi:10.1016/j.joei.2023.101252.
13. Veiga, S.; Romero, M.; Faccio, R.; Segobia, D.; Apesteguia, C.; Perez, A. L.; Brondino, C. D.; Bussi, J. Biogas dry reforming over Ni-La-Ti catalysts for synthesis gas production: Effects of preparation method and biogas composition. *Fuel* **2023**, 346, doi:10.1016/j.fuel.2023.128300.
14. Cherbanski, R.; Kotkowski, T.; Molga, E. Thermogravimetric analysis of coking during dry reforming of methane. *International Journal of Hydrogen Energy* **2023**, 48, 7346-7360.
15. Nishimura, A.; Yamada, S.; Ichii, R.; Ichikawa, M.; Hayakawa, T.; Kolhe, M. L. Hydrogen yield enhancement in biogas dry reforming with a Ni/Cr catalyst: A numerical study. *energies* **2024**, 17, doi:10.3390/en17215421.
16. Jokar, S. M.; Farokhnia, A.; Tavakolian, M.; Pejman, M.; Parvasi, P.; Javanmardi, J.; Zare, F.; Clara Goncalves, M.; Basile, A. The recent areas of applicability of palladium based membrane technologies for hydrogen production from methane and natural gas: a review. *International Journal of Hydrogen Energy* **2023**, 48, 6451-6476.
17. Bang, G.; Moon, D. K.; Kang, J. H.; Han, Y. J.; Kim, K. M.; Lee, C. H. High-purity hydrogen production via a water-gas-shift reaction in a palladium-copper catalytic membrane reactor integrated with pressure swing adsorption. *Chemical Engineering Journal* **2021**, 411, doi:10.1016/j.cej.2021.128473.
18. Lee, S.; Lim, H. The power of molten salt in methane dry reforming: Conceptual design with a CFD study. *Chemical Engineering Process.-Process Intensif.* **2021**, 159, doi:10.1016/j.cep.2020.108230.
19. Lee, S.; Lim, H. The effect of changing the number of membranes in methane carbon dioxide reforming: A CFD study. *International Journal of Engineering Chemistry*. **2020**, 87, 110-119.
20. Ghasemazadeh, K.; Ghahremani, M.; Amiri, T. Y.; Basile, A. Performance evaluation of Pd-Ag membrane reactor in glyceol steam reforming process: Development of the CFD model. *International Journal of Hydrogen Energy* **2019**, 44, 1000-1009.
21. Lee, B.; Lee, S.; Lim, K.; Numerical modeling studies for a methane dry reforming in a membrane reactor. *J. Nat. Gas. Sci. Eng.* **2016**, 34, 1251-1261.
22. Nishimura, A.; Mishima, D.; Ito, S.; Konbu, T.; Hu, E. Impact of separator thickness on relationship between temperature distribution and mass & current density distribution in single HT-PEMFC. *Thermal Science Engineering* **2023**, 6, doi:10.24294/tse.v6i2.4424.
23. Nishimura, A.; Ito, S.; Ichikawa, M.; Kolhe, M. L. Impact of thickness of Pd/Cu membrane on performance of biogas dry reforming membrane reactor utilizing Ni/Cr catalyst. *fuels* **2024**, 5, 439-457.
24. Nishimura, A.; Ichikawa, M.; Yamada, S.; Ichii, R. The characteristics of a Ni/Cr/Ru catalyst for a biogas dry reforming membrane reactor using a Pd/Cu membrane and a comparison of it with a Ni/Cr catalyst. *hydrogen* **2024**, 5, 414-435.
25. Lee, S.; Lim, H. The power of molten salt in methane dry reforming: conceptual design with a CFD study. *Chemical Engineering and Processing* **2020**, 159, doi:10.1016/j.cep.2020.108230.
26. Amini, A.; Sedaghat, M. H.; Jamshidi, S.; Shariati, A.; Rahimpour, M. R. A Comprehensive CFD simulation of an industrial-scale side-fired steam methane reformer to enhance hydrogen production. *Chemical Engineering and processing* **2023**, 184, doi:10.1016/j.cept.2023.109269.
27. Bengerbaa, Y.; Virginieb, M.; Dumas, C. Computational fluid dynamics study of the dry reforming of methane over Ni/Al₂O₃ catalyst in membrane reactor – coke deposition. *Kinetic and Catalysis* **2017**, 58, 345-355.
28. Kaviani, M.; Rezaei, M.; Alavi, S. M.; Akbari, E. Biogas dry reforming over nickel-silica sandwiched core-shell catalyst with various shell thickness. *Fuel* **2024**, 355, doi:10.1016/j.fuel.2023.129533.
29. Georgiadis, A. G.; Siakavelas, G. I.; Tsiotsias, A. I.; Charisous, N. D.; Ehrhardt, B.; Wang, W.; Sebastian, V.; Hinder, S. J.; Baker, M. A.; Mascotto, S.; Goula, M. A. Biogas dry reforming over Ni/LnO_x-type catalysts (Ln = La, Ce, Sm or Pr). *International Journal of Hydrogen Energy* **2023**, 48, 19953-19971.
30. Martin-Espejo, J. L.; Merkouri, L. P.; Gandara-Loe, J.; Odriozola, J. A.; Reina, T. R.; Pastor-Perez, L. Nickel-based cerium zirconate inorganic complex structures for CO₂ valorisation via dry reforming of methane. *Journal of Environmental Sciences* **2024**, 140, 12-23.
31. Kiani, P.; Meshksar, M.; Rahimpour, M. R. Biogas reforming over La-promoted Ni/SBA-16 catalyst for syngas production: Catalytic structure and process activity investigation. *International Journal of Hydrogen Energy* **2023**, 48, 6262-6274.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.