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Effect of Oxidants on Syngas Synthesis from Biogas over 3 wt % Ni-Ce-MgO-ZrO₂/Al₂O₃ Catalyst

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Abstract: The utilization of fossil fuels has led to a gradual increase in greenhouse gas emissions, which have accelerated global climate change. Therefore, there is a growing interest in renewable energy sources and technologies. Biogas has gained considerable attention as an abundant renewable energy resource. Common biogases include anaerobic digestion gas and landfill gas, which can be used to synthesize high-value-added syngas through catalytic reforming. Because syngas (CO and H₂) is synthesized at high reaction temperature, carbon is generated by the Boudouard reaction from CO and CH₄ cracking; thus, C blocks the pores and surface of the catalyst, thereby causing catalyst deactivation. In this study, a simulation was performed to measure the CH₄ and CO₂ conversion rates and the syngas yield for different ratios of CO₂/CH₄ (0.5, 1, and 2). The simulation results showed that the optimum CO₂/CH₄ ratio is 0.5; therefore, biogas reforming over the 3 wt% Ni/Ce-MgO-ZrO₂/Al₂O₃ catalyst was performed under these conditions. CH₄ and CO₂ conversion rates and the syngas yield were evaluated by varying the R values (R = (CO₂ + O₂)/CH₄) on the effect of CO₂ and O₂ oxidants of CH₄. In addition, steam was added during biogas reforming to elucidate the effect of steam addition on CO₂ and CH₄ conversion rates. The durability and activity of the catalyst after 200-h biogas reforming were evaluated under the optimal conditions of R = 0.7, 850 °C, and 1 atm.

Keywords: biogas; reforming; syngas synthesis; Ni catalysts; carbon dioxide

1. Introduction

Owing to concern regarding the effects of climate change, many countries signed the “Paris Agreement” in 2015, agreeing to reduce greenhouse gas (GHG) emissions and limit the increase in global temperatures to below 1.5 °C [1,2]. Since then, energy conversion technologies such as carbon capture and storage (CCS) and carbon capture and utilization (CCU) have been gaining momentum in different countries as a means for sustainable utilization of energy sources and reduction of GHG emissions [3]. In particular, biomass fuel, which has the potential to reduce GHG emissions, can be easily obtained from trees, farming byproducts, livestock waste, and urban solid waste. Organic waste is a sustainable energy source, whose availability can increase with economic growth and population.

It is known that biogas produced from anaerobic digestion consists mainly of CO₂ and CH₄; however, the ratio of CO₂ to CH₄ varies depending on the source of the biogas. Anaerobic digestion gas (ADG), produced from sewage sludge or manure, is composed of 60–80% CH₄ and 20–40% CO₂, while landfill gas (LFG) is comprised of 40–60% CH₄ and 40–60% CO₂.

Raw biogas is subjected to purification to remove impurities (such as H₂S, H₂O, and siloxane). Subsequently, CO₂ and highly concentrated CH₄ are separated, so that CH₄ can be utilized as fuel [4].
In addition to being used as a fuel, syngas is synthesized by catalytic reforming to produce high-value-added chemicals, thus contributing immensely to the reduction of GHG emissions [5]. Syngas is currently produced mostly through CH\textsubscript{4} reforming of natural gas (NG). However, biogas is an affordable and suitable raw material for syngas production. Biogas can be converted into methanol, acetic acid, dimethyl ether (DME), ammonia, and the Fischer-Tropsch oil, which are high-value-added products [6].

Dry reforming of CH\textsubscript{4} and CO\textsubscript{2} has a low H\textsubscript{2}/CO ratio (i.e., 1). Steam reforming from CH\textsubscript{4} and H\textsubscript{2}O has a higher H\textsubscript{2}/CO ratio (i.e., 3) due to the presence of hydrogen in water. Tri-reforming involves the addition of O\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O to CH\textsubscript{4}, but does not generate as much carbon deposit as dry reforming. H\textsubscript{2}O and O\textsubscript{2} serve as oxidizing agents, converting the carbon deposit into CO and CO\textsubscript{2}. Thus, H\textsubscript{2}O and O\textsubscript{2} prevent the rapid catalyst deactivation due to carbon formation.

As biogas reforming proceeds, sulfur coverages toward the exit-side of the reactor increase. Operating the reactor at high temperatures can significantly reduce sulfur adsorption. Consequently, catalyst saturation and sulfur coverages are lower than those for low-temperature operation. Sulfur absorption is mainly attributable to the sticking and desorption reactions of H\textsubscript{2}S. An increase in the sticking coefficient for H\textsubscript{2}S results in higher sulfur coverages, whereas an increase in the H\textsubscript{2}S desorption pre-exponential factor results in lower sulfur coverage over Ni-based catalysts. In addition to these reactions, hydrogen abstraction from H\textsubscript{2}S and the reaction between absorbed H\textsubscript{2}S and O influence the formation of absorbed sulfur. Appari et al. [7] reported that before the introduction of H\textsubscript{2}S into the feed, CO and H are the main species adsorbed on the catalyst surface, and most of the catalyst surface remains available for adsorption. As soon as H\textsubscript{2}S is introduced, sulfur begins to occupy most of the catalyst surface and CO and H coverages begin to decrease.

Catalysts for the reforming reaction include precious metals, spinel, perovskites, and mesoporous catalysts. These catalysts can be categorized based on the metal type, preparation method, and structure. Catalysts based on precious metals have high activity and resistance to carbon formation but are typically expensive [8]. Ni- and Co-based catalysts show high activity, similar to those of precious metal catalysts; however, the use of Ni can lead to the rapid catalyst deactivation due to carbon deposition and sintering [9]. Precious and non-precious metals are mainly used for the activation of catalysts. Ni-based catalysts have been widely commercialized and are used for activation in steam reforming.

Precursors (CeO\textsubscript{2} and ZrO\textsubscript{2}) for Ni- and Co-based catalysts include oxygen, which can prevent catalyst deactivation because carbon is oxidized by oxygen. ZrO\textsubscript{2} reduces NiO to Ni, while preventing the formation of deactivated Ni\textsubscript{2}O\textsubscript{3} [10]. Carbon is known to form on the acidic surface of the support, and the use of basic co-catalysts (CaO, MgO) can improve the resistance to carbon formation [11]. MgO reportedly enhances the binding force in the presence of NiO, which improves the resistance of Ni-based catalysts to sintering and carbon formation and facilitates the highest catalytic performance [12].

Due to their redox properties and oxygen storage capacity, Ni-based catalysts supported on CeO\textsubscript{2} or CeO\textsubscript{2}-ZrO\textsubscript{2} mixed oxides show promising performance, as well as low coke formation. Additionally, catalysts containing more than one active species have been recently investigated. The use of CeO\textsubscript{2} as a support promotes the action of precious metals by preventing the sintering of Pt metal particles and ensuring high dispersion of the active component over the support. Trutchetti et al. [13] studied the kinetics of CH\textsubscript{4} steam reforming over Ni-based catalysts and confirmed that the activation energy of the Pt-added catalyst was lower than that when the Pt-added Ni-based catalyst was supported on CeO\textsubscript{2} and Ce-Zr-La. Sunarno et al. [14] showed that the rate constants of the catalytic cracking of bio-oil increased with an increasing temperature. The reaction rate constants of the catalytic cracking of bio-oil using Model 1 ranged from 0.221 to 0.416 cm\textsuperscript{3}/g cat-min with an activation energy of 22.3 kJ/mol.

The biogas reforming experiment over the 3 wt% Ni/Ce-MgO-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst was performed under these conditions. CH\textsubscript{4} and CO\textsubscript{2} conversion rates and syngas yield were evaluated by varying the R values (R = (CO\textsubscript{2} + O\textsubscript{2})/CH\textsubscript{4}) on the effects of CO\textsubscript{2} and O\textsubscript{2} as oxidants of CH\textsubscript{4}. In addition, steam was added during biogas reforming to elucidate its effect on CO\textsubscript{2} and CH\textsubscript{4} conversion rates. The
durability and activity of the catalyst after 200-h biogas reforming were evaluated under the optimal conditions of $R = 0.7$, 850 °C, and 1 atm.

2. Biogas Reforming Reaction

2.1. Reaction Mechanism

Biogas reforming involves a high-temperature reaction to obtain syngas ($\text{H}_2$ and CO) as an endothermic reaction product of $\text{CH}_4$ and $\text{CO}_2$ [15]. Biogas reforming occurs through mechanisms similar to those of dry and wet reforming, as well as tri-reforming [16].

As shown in Table 1, dry reforming involves the reaction between $\text{CH}_4$ and $\text{CO}_2$ and can be utilized to produce syngas from biogas (Number 1, Table 1). Other side reactions that might occur include the reverse water–gas shift (RWGS) reaction (Number 2), methanation (Number 3 and 4), Boudouard reaction (Number 5), carbon oxidation (Number 6), carbon gasification (Number 7), and $\text{CH}_4$ cracking (Number 8). The reaction performance has an effect on the $\text{H}_2$/CO ratio [17].

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$\Delta H_{298}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2$</td>
<td>247.0</td>
</tr>
<tr>
<td>2</td>
<td>$\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$</td>
<td>41.0</td>
</tr>
<tr>
<td>3</td>
<td>$\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$</td>
<td>−206.2</td>
</tr>
<tr>
<td>4</td>
<td>$\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}$</td>
<td>165.0</td>
</tr>
<tr>
<td>5</td>
<td>$2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$</td>
<td>−172.4</td>
</tr>
<tr>
<td>6</td>
<td>$\text{C} + 1/2\text{O}_2 \leftrightarrow \text{CO}$</td>
<td>110.0</td>
</tr>
<tr>
<td>7</td>
<td>$\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2$</td>
<td>131.0</td>
</tr>
<tr>
<td>8</td>
<td>$\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2$</td>
<td>74.9</td>
</tr>
<tr>
<td>9</td>
<td>$\text{CH}_4 + 1/2\text{O}_2 \leftrightarrow \text{CO} + \text{H}_2$</td>
<td>−36.0</td>
</tr>
<tr>
<td>10</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$</td>
<td>206.2</td>
</tr>
<tr>
<td>11</td>
<td>$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO} + 4\text{H}_2$</td>
<td>164.9</td>
</tr>
<tr>
<td>12</td>
<td>$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$</td>
<td>−41.2</td>
</tr>
<tr>
<td>13</td>
<td>$\text{CO} + 1/2\text{O}_2 \leftrightarrow \text{CO}_2$</td>
<td>−283.0</td>
</tr>
<tr>
<td>14</td>
<td>$\text{H}_2 + 1/2\text{O}_2 \leftrightarrow \text{H}_2\text{O}$</td>
<td>−241.8</td>
</tr>
</tbody>
</table>

When the RWGS reaction occurs during biogas reforming, the $\text{CO}_2$ conversion rate tends to increase, and the carbon that is formed from the Boudouard and $\text{CH}_4$ cracking reactions is deposited in the pores of the catalyst. According to Wang et al. [18], $\text{CH}_4$ cracking, which involves the decomposition of $\text{CH}_4$, occurs above 557 °C, whereas the Boudouard reaction, which involves the formation of carbon from $\text{CO}$, occurs below 700 °C. Additionally, other reactions that yield carbon between 557–700 °C take place and block the catalyst pores, decreasing catalytic performance. The work of Jang W.J. et al. [19] and D.G. Avraam [20] confirmed that steam addition during reforming can prevent carbon formation.

Moreover, $\text{O}_2$ in biogas serves as an oxidizing agent for $\text{CH}_4$ to produce $\text{H}_2$ and CO through partial oxidation (Number 9). When both $\text{CH}_4$ and $\text{O}_2$ are present, an autothermal reaction (ATR) occurs, which can provide heat that facilitates $\text{CO}_2$ reforming of $\text{CH}_4$ (Number 1), which is an endothermic reaction.

Li et al. [21] and Amin et al. [22] reported that $\text{O}_2$ serves as an oxidizing agent for $\text{CH}_4$ in the beginning followed by $\text{CO}_2$; thus, the amount of $\text{O}_2$ in biogas has an effect on the $\text{CH}_4$ and $\text{CO}_2$ conversion rates. The addition of water to biogas favors a highly endothermic reaction, which produces syngas through a reforming reaction between $\text{CH}_4$, $\text{CO}_2$, and steam, as well as via other reactions that occur simultaneously (Number 10–12). The addition of water facilitates the water–gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) and increases the $\text{H}_2$ concentration in syngas but reduces the reaction rate because it is an endothermic reaction. The reaction caused by steam addition requires heat, which is supplemented by a heater, or heat is provided by the ATR reaction induced by $\text{O}_2$ [23]. From the
simulation result obtained by Avraam D.G. et al. [21] and Huang C. et al. [24], a similar effect of steam was observed for these reactions under the same experimental conditions.

2.2. Reaction Simulation

Dry reforming simulations based on the Gibbs reactor method were performed at CO₂/CH₄ ratios of 0.5, 1.0, or 2.0 by using PRO/II simulator (Ver. 9.4). Figure 1a displays the CO₂ and CH₄ conversion rates, and Figure 1b shows the changes in the H₂/CO ratio as a function of the reaction temperature. The CH₄ conversion rate was the highest for the CO₂/CH₄ ratio of 0.5 and remained almost unchanged above 800 °C (Figure 1a) [25]. The CO₂ conversion rate was the highest for the CO₂/CH₄ ratio of 0.5 and was more than 90% above 850 °C (Figure 1b). As the temperature increased, the H₂/CO ratio decreased slightly. The lower the CO₂/CH₄ ratio, the higher the H₂/CO ratio is for 0.8, 1, and 1.5. When the CO₂/CH₄ ratio was 0.5, the CO₂ and CH₄ conversion rates were the highest, and the experiment was carried out at CO₂/CH₄ ratio of 0.5 (Figure 1b). The CO₂ and CH₄ conversion rates for the CO₂/CH₄ ratio measured in this study were in good agreement with the data reported by Istadi et al. [26], and the simulation results were similar to those reported by Nikoo et al. [27].

![Figure 1](image.png)

**Figure 1.** (a) Effects of CO₂/CH₄ ratio on CO₂ and CH₄ conversion rates during a simulated biogas reforming reaction; (b) Effects of CO₂/CH₄ ratio on H₂/CO ratio during a simulated biogas reforming reaction.

2.3. Research Overview

The relationship between the amounts of oxidizing agents (CO₂ and O₂) in CH₄ and CH₄ was investigated. Figure 2a shows the effect of oxidants on the yields of H₂ and CO at 180 cc/min (R = 0.74) and 195 cc/min (R = 0.8). When the proportion of CO₂ was increased (the amount of O₂ was decreased) in the same amount of the oxidizing agent, the yields of H₂ and CO remained almost unchanged. When the flow rate of the O₂ or CO₂ oxidant is constant, the change in the R value is >1, as shown in Figure 2b. There is little effect on the CH₄ selectivity and the yield of H₂ and CO produced; however, the CO₂ conversion rate decreases as CO₂ decreases and O₂ increases. It is thought that the conversion rate decreases with the ratio of CO₂ in the reactants. Because the effects of oxidants CO₂ and O₂ are similar to those of CH₄ and CO₂, the effects of O₂ and CO₂ as a factor of CH₄ oxidants were analyzed for a CO₂/CH₄ ratio of 0.5. In addition, when R ≥ 1, because the CO₂ conversion rate is considerably reduced [25,28], the effect of the oxidizing agent at R < 1 will be examined.
1 and 15 atm. The gas hourly space velocity (GHSV) was calculated using Equation (1), where

\[ \text{GHSV} = \frac{Q}{V} \]  


As mentioned above, the experiment was carried out for a CO\textsubscript{2}/CH\textsubscript{4} ratio of 0.5. Additionally, the amounts of CO\textsubscript{2} and O\textsubscript{2}, which serves as an oxidant for CH\textsubscript{4}, were defined as \( R = (\text{O}_2 + \text{CO}_2)/\text{CH}_4 \). The \( R \) value was varied between 0.6, 0.7, and 0.9 in the experiments (Table 2). Furthermore, steam was added at a flow rate of 125 cc/min to examine the effect of steam addition on biogas reforming.

3. Catalyst and Reaction Experiment

3.1. Experimental Apparatus and Method

The experimental apparatus is shown in Figures 3 and 4. In the experiment, 4 g of catalyst was placed in the middle of a reactor with an inner diameter of 25 mm and length of 150 mm. The reactor temperature was controlled by an electrical furnace, and the reactor pressure was maintained between 1 and 15 atm. The gas hourly space velocity (GHSV) was calculated using Equation (1), where \( Q \) is the volumetric flow rate and \( V \) is the volume of the catalyst. The biogas was mixed with the simulated gas. As mentioned above, the experiment was carried out for a CO\textsubscript{2}/CH\textsubscript{4} ratio of 0.5. Additionally, the amounts of CO\textsubscript{2} and O\textsubscript{2}, which serves as an oxidant for CH\textsubscript{4}, were defined as \( R = (\text{O}_2 + \text{CO}_2)/\text{CH}_4 \). The \( R \) value was varied between 0.6, 0.7, and 0.9 in the experiments (Table 2). Furthermore, steam was added at a flow rate of 125 cc/min to examine the effect of steam addition on biogas reforming.
3.2. Catalyst Preparation and Analysis of Properties

The catalyst was prepared, as illustrated in Figure 5, by using the appropriate amount of γ-Al₂O₃ as the support for loading and preparing a slurry of zirconium nitrate (Zr(NO₃)₄) and cerium acetate hydrate (CH₃CO₂)₃Ce·6H₂O. The slurry was evenly mixed at 500 rpm and stabilized at 40 °C to produce Solution (1). Solution (1) was sintered at 900 °C for 3 h in a sintering furnace to obtain powder (1). Next, Solution (2) was converted to a slurry by mixing nickel (II) nitrate solution and magnesium nitrate. Solution (2) was impregnated with powder (1) and sintered at 750 °C for 6.5 h in the sintering furnace to obtain 3 wt% Ni/Ce-MgO-ZrO₂/Al₂O₃ catalyst [29,30].

Table 2. Experimental conditions for biogas reforming.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Component</th>
<th>CH₄ (mL/min)</th>
<th>CO₂ (mL/min)</th>
<th>O₂ (mL/min)</th>
<th>Steam (mL/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td></td>
<td>120</td>
<td>60</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td></td>
<td>120</td>
<td>60</td>
<td>24</td>
<td>125</td>
</tr>
<tr>
<td>0.9</td>
<td></td>
<td>120</td>
<td>60</td>
<td>48</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Preparation of the 3 wt% Ni-catalyst.
The catalyst powder was pre-treated at 250 °C for 5 h, and its composition was evaluated by X-ray diffraction (XRD, Philips PW1800; Figure 6). The radioactive source used was Cu-K radiation with a scanning speed of 2θ = 4°/min, an output of 40 kV, and a current of 100 mA [31,32]. Figure 6a shows the XRD pattern for the catalyst before the reforming reaction, and Figure 6b displays the XRD pattern measured after a 200-h reforming reaction. The NiO peak (2θ value), which corresponds to the active site of the catalyst, is observed at 37.2° and 43.3° (Figure 6a,b, respectively). After 200-h reforming, although it was not possible to determine the exact 2θ values, the NiO and Al2O3 peaks were found to overlap at 43.3° and the NiO intensity was found to decrease at 37.2°. It is believed that NiO crystals increase in size and have lower intensity at higher temperatures [33]. To analyze the properties of the catalyst surface, the specific surface area during the physisorption of N2 (−196 °C) at 300 °C was measured using the Brunauer–Emmett–Teller (BET) method. The catalyst surface was characterized by BET (ASAP2020 Plus version 1.02, Micromeritics) at the center for advanced materials analysis at Suwon University. The specific surface area and pore sizes of the catalyst are listed in Table 3. No change in the BET value was observed after 200-h reforming, which confirms that the surface area remained largely unchanged even after a long-term stability test was performed [34].

![Figure 6. XRD patterns of the 3 wt% Ni/Ce-MgO-ZrO2/Al2O3 catalyst: (a) before reforming and (b) after 200-h reforming.](image)

<table>
<thead>
<tr>
<th>BET (m²/g)</th>
<th>Pore Size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>2.94</td>
</tr>
<tr>
<td>After</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 3. Surface area and pore size of the 3 wt% Ni/Ce-ZrO2/Al2O3 catalyst before and after reforming.

Table 4 summarizes the composition of the catalyst determined by ICP-OES. The contents of Ce and MgO in the catalyst decreased slightly, while those of NiO and Zr remained consistent after
reforming. Figure 7 shows a scanning electron microscopy (SEM) image of the catalyst surface, which confirms that the catalyst has a relatively even particle size and shape [35].

Table 4. Composition of the 3 wt\% Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst before and after reforming.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ce</th>
<th>MgO</th>
<th>NiO</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before (wt %)</td>
<td>1.3</td>
<td>3.1</td>
<td>3.5</td>
<td>2.6</td>
</tr>
<tr>
<td>After (wt %)</td>
<td>0.8</td>
<td>1.7</td>
<td>3.7</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Figure 7. SEM image of the 3 wt\% Ni/Ce-ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst.

4. Result and Discussion

4.1. Effect of Temperature on CH\textsubscript{4} and CO\textsubscript{2} Conversion Rates

In biogas reforming, the $R$ value was set to 0.7, which was close to the stoichiometric ratio. The effect of temperature on the CH\textsubscript{4} and CO\textsubscript{2} conversion rates and syngas yield are shown in Figure 8. With the increase in temperature, the CO\textsubscript{2} conversion rate increased and the CH\textsubscript{4} conversion rate was close to 100%. As the temperature increased, the syngas yield (H\textsubscript{2} + CO) increased. The activity increases with increasing temperature, and the yield of syngas seems to increase slightly [36].

Figure 8. Effect of temperature on CO\textsubscript{2} and CH\textsubscript{4} conversion rates during biogas reforming at $R = 0.7$ (O\textsubscript{2}/CH\textsubscript{4} = 0.2).


4.2. Effect of R Value on CH₄ and CO₂ Conversion Rates

The effect of the R value (0.6, 0.7, and 0.9) on the CH₄ and CO₂ conversion rates is shown in Figure 9. The CH₄ conversion rate is close to 100% regardless of the R value. This result is similar to that reported by Li et al. [21]. However, the CO₂ conversion rate is 98% at the R value of 0.7 and decreases with higher R values. As the R value increases, the amount of O₂ increases and CO and C generated from CH₄ react with O₂ to produce CO₂, which can be attributed to the decrease in the CO₂ conversion rate [37].

![Figure 9. Effect of R values on CO₂ and CH₄ conversion rates.](image)

4.3. Effect of R Values on H₂ and CO Yields

The effect of the R values on the syngas yield is illustrated in Figure 10. As the R value increased, the CO concentration increased; however, when the R value was greater than 0.7, the yield tended to be constant. It is believed that the R value increases because of the increase in the ratio of the oxidant and CO, and the resulting CO will react with oxygen and re-oxidize to CO₂ after the R value has reached 0.7. Because CO₂ is formed due to the reaction between CH₄ and O₂ owing to an increase in the amount of oxygen when the R value is higher than 0.7, the amount of CO produced from CO₂ will decrease.

![Figure 10. Effect of R = ([O₂ + CO₂]/CH₄) values on syngas yield.](image)
The H₂ concentration increases with the R value and reaches ~50%. As the R value increases, the amounts of CO and H₂ produced increase due to the oxidation reaction of CH₄. Whereas, when the R value is greater than 0.7, the amount of H₂ is considered to decrease because of the reaction with O.

4.4. Effect of Steam on CH₄ and CO₂ Conversion Rates

The effect of steam on the biogas reforming reaction is shown in Figures 11 and 12. The CH₄ conversion rate was close to 100% at 750 °C and 850 °C, regardless of the R value. It is believed that adequate amount of O in the steam could have increased the CH₄ conversion rate. On the other hand, the decrease in the CO₂ conversion rate is due to the increase in the number of O molecules owing to the increase in the R value, compared to the stoichiometric ratio. Thus, because of the increase in the amount of O, the re-oxidation reaction with CO occurs. With the increase in the R value, the CO concentration remains almost unchanged; the H₂ concentration, which remains constant at 750 °C, tends to decrease at 850 °C. It is believed that H₂ produced from CH₄ reacts with O₂ at 850 °C to produce H₂O, which in turn reduces the yield of H₂.

![Figure 11](image1.png)

**Figure 11.** Effect of \( R = ((O_2 + CO_2)/CH_4) \) values on H₂ and CO formation with steam addition.

![Figure 12](image2.png)

**Figure 12.** Effect of \( R = ((O_2 + CO_2)/CH_4) \) values on H₂ and CO formation with steam addition.

Comparison of the biogas reforming reactions with and without steam addition indicates that the amounts of H₂ and O₂ increased because of steam addition, the CH₄ conversion rate increased because
of oxidation, and the CO₂ conversion rate decreased because of the presence of adequate O owing to the oxidation of CO. This result is similar to that reported by Song CS et al. [38].

4.5. Synthesis of Chemicals with the Value of H₂/CO Ratio

Figure 13 shows the H₂/CO ratios in the dry reforming and wet reforming. The reactions for DME and methanol syntheses were performed according to the H₂/CO ratio of the syngas. In the case of dry reforming, the H₂/CO ratio is ~1.2 to 1.6, which is the highest when the R value is lower. In the case of wet reforming, the H₂/CO ratio is ~2.0. Thus, wet reforming results in a higher H₂/CO ratio than dry reforming because a larger amount of H₂ is produced from steam.

![Figure 13.](image)

The syngas produced by dry reforming is suitable for the generation of high-value-added products through DME synthesis at the stoichiometric ratio (H₂/CO = 1). In the case of wet reforming, the H₂/CO ratio is ~2; thus, methanol can be produced through methanol synthesis in which the stoichiometric ratio of H₂/CO is 2. Therefore, DME and methanol syntheses were carried out over the Cu-ZnO/γ-Al₂O₃ catalyst. The experiment was conducted at 60 bars in the temperature range of 200–300 °C. The effects of the H₂/CO ratio on DME and methanol yields were analyzed (Figure 14). The DME yield was the highest for the H₂/CO ratio of 1.0–1.2, and it decreased when the ratio was higher than 1.2. Therefore, dry reforming can be used for the DME synthesis, as mentioned previously.

![Figure 14.](image)
4.6. Durability and Activity of Catalyst

To evaluate the durability and activity of the catalyst, a 200-h reforming experiment under the optimized conditions \((R = 0.7, 845 \degree C)\) was conducted. As shown in Figure 15, 42% H₂, 45% CO, and a constant CH₄ conversion rate of ~99% were obtained. On the other hand, CO₂ has a tendency to maintain a conversion rate of up to 97%, which may decrease slightly. It is believed that the durability and activity of 200-h biogas reforming over the 3 wt% Ni/ Ce-MgO-ZrO₂/Al₂O₃ catalyst are well maintained.

![Figure 15. Durability of over 3 wt% Ni/ Ce-MgO-ZrO₂/Al₂O₃ for 200-h biogas reforming reaction.](image)

5. Conclusions

This study achieves \(R\) values (0.6, 0.7, and 0.9; where \(R = ((O_2 + CO_2)/CH_4)\)) for biogas reforming over the 3 wt% Ni/ Ce-MgO-ZrO₂/Al₂O₃ catalyst. The following are the main conclusions:

1) In the biogas reforming reaction simulation, the highest CO₂ and CH₄ conversion rates were obtained for the CO₂/CH₄ ratio of 0.5. Under this condition, the CH₄ conversion rate was close to 100% for the R value of 0.7, and the CO₂ conversion rate was close to 98%.

2) The CH₄ conversion rate was close to 100% regardless of the R value, and the CO₂ conversion rate decreased as the R value increased. The amount of O₂ increases with the R value, and CO and C formed from CH₄ react with O₂ to produce CO₂, which in turn decreases the CO₂ conversion rate.

3) As the amount of O₂ increases with the R value during biogas reforming, the amount of H₂ formed increased initially, and then decreased after reaching the R value of 0.7, because H₂O was formed from the reaction between oxygen and H₂. Meanwhile, the amount of CO decreased as it was re-oxidized to CO₂.

4) Upon investigating the effect of steam addition on the reforming reaction, the CH₄ conversion rate was close to 100% regardless of the R value, and the CO₂ conversion rate decreased due to the re-oxidation of CO. The H₂ concentration showed a decrease at 850 °C as the R value increased. In the reforming reaction where steam was added to biogas, the CO concentration increased, whereas the H₂ concentration increased.

5) Although the DME yield decreased above the H₂/CO ratio of 1.2 during biogas reforming, it showed the highest value at the H₂/CO ratio of 1.0–1.2.

6) The stability of the 3 wt% Ni/ Ce-MgO-ZrO₂/Al₂O₃ catalyst was evaluated at 845 °C for 200 h biogas reforming. It was found that the CH₄ conversion rate remained constant at ~99%, and the CO₂ conversion rate remained at ~97%. Therefore, the catalyst is expected to maintain high stability.
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