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Evaluation of a Sabatier Reaction Utilizing Hydrogen Produced by Concentrator Photovoltaic Modules under Outdoor Conditions

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Abstract: Power to gas (P2G) process chains have tremendous potential to enhance energy systems because of the capability of solar energy to convert solar radiation into electrical energy as well as the increasing use of specific gases as a means to store the resulting energy. Utilizing sunlight, photovoltaic systems are capable of producing useful gases such as hydrogen (H_2) and methane (CH_4). These gases are utilized in gas grids, transportation, and heavy industry. In employing a sunlight-derived gas, H_2 production, by water disbanding, needs to be cost-effective with tremendous adaptability. New powerful solar to gas conversion system modules have been successfully carried out in the University of Miyazaki, Japan. These systems contain DC/DC converters and electrolyzer sets linked in parallel with efficient three concentrator photovoltaics (CPV). The performance of the solar to methane conversion process and power consumption analysis will be the focus of the current research. Efficiencies of 97.6% of CO_2 to CH_4 conversion and 13.8% for solar to methane on a clear sunny day were obtained by utilizing highly efficient CPV modules connected with multiple converters, electrochemical cells, and reactors fixed with Ni-based catalysts.

Keywords: concentrator photovoltaic; DC/DC converter; hydrogen generation; Ni-based catalyst; proton exchange membrane electrolysis; solar to gas; Sabatier process; water electrolysis

1. Introduction

Increasing greenhouse gas emissions around the world has become a matter of paramount importance in today's energy production scenario. A reduction of carbon dioxide (CO_2) emissions resulting from energy production is a common objective in industry and research. The conversion of CO_2 into artificial methane (CH_4) by catalytic reaction of thermodynamic methanation is a sustainable technique currently gaining attention in the solar to methane (StM) chain technical community. Electrical energy from renewable sources can be converted into storable chemical energy. A potential solution for solar energy storage is the transformation of solar energy into synthetic chemical energy. The transformation can be accomplished by a Sabatier reaction. In this reaction, a catalytic methanation is performed by the combination of carbon dioxide (CO_2) and hydrogen (H_2) produced from water splitting and possibly from a renewable energy source. Highly efficient concentrator photovoltaic (CPV) modules (as a renewable energy source) and electrochemical (EC) cells for H_2 production are compulsory for efficient conversion of solar energy to H_2 gas [1]. A CPV system with the highest efficiency is one of the crucial aspects in the development of a modernized solar system. One of the most

up-and-coming technologies in the conversion of solar energy to chemical energy is the combination of solar energy to H_2 and CO_2 gases in the methanation process. This synthetic natural gas could be substituted in the current gas grid sector since CH_4 can be stored effectively. According to the measurements done by the state of the art, the best efficiencies in the various studies were achieved to 90% for the capture of CO_2 from off-gas [2], 80% for water electrolysis [3], and 80% for CO_2 methanation [4]. The combination of sunlight-derived hydrogen and CO_2 to store solar energy in the chemical form of CH_4 with higher efficiency is still in the development stage. Therefore, in this study, the produced hydrogen from the efficient CPV modules under outdoor conditions was directly applied to the methanation system, and the conversion efficiency and power consumption of solar to methane were considered and evaluated.

Figure 1 shows the fundamental StM concept of our system. As shown in Figure 1, sunlight was captured by highly efficient CPV modules and transformed into high-grade solar energy. The produced electrical energy was utilized in the water splitting system (which consisted of EC cells and DC/DC converters) to convert to H_2 and oxygen. The proton exchange membrane (PEM) electrolysis method is currently attracting researchers' attention as a result of its higher resilience, high functioning current densities, authentic gas generation, H_2 manufacturing at a higher pressure, and compact structure. The process of mixing H_2 and CO_2 gases occurs while producing CH_4 within the reactors. The energy conversion efficiency from solar to hydrogen and composition of produced methane can be unique depending upon the types of water splitting system, reactors, and catalysts.
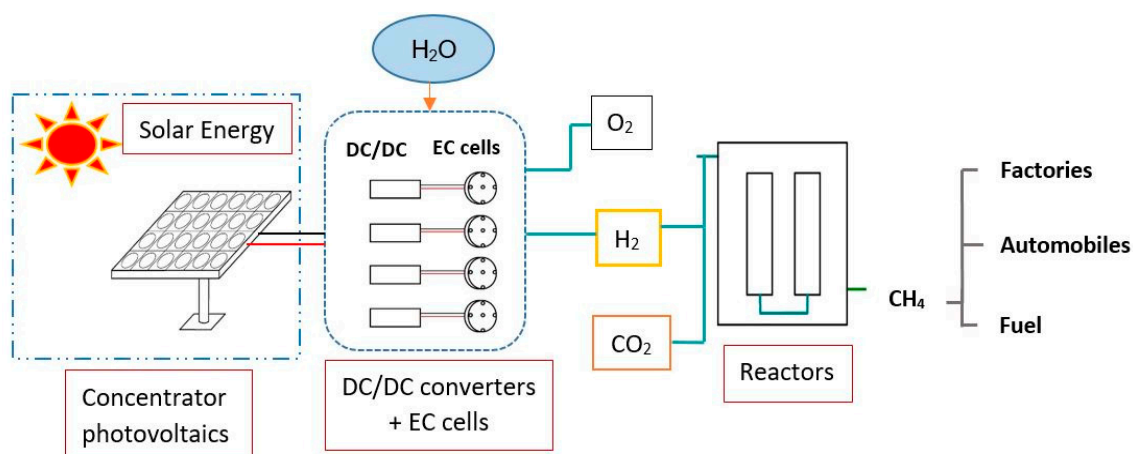

Figure 1. Schematic illustration of the fundamental solar to methane (StM) concept of our system.

The conversion of CO_2 to CH_4 in the presence of a catalyst (usually a Ni-based catalyst) and at a temperature of 250 to 300 °C has the characteristics of a thermochemical or thermocatalytic methanation [5]. The procedure of hydrogenating CO_2 to get synthetic CH_4 natural gas is mostly referred to as the Sabatier process. A highly effective catalyst is required for the direct conversion of CO_2 to CH_4 with a reasonable conversion rate. The catalyst also enables selectivity at specified lower temperatures while providing no evidence of transitional conditions [6,7]. The state of the art Ni-based catalyst is the preferred active catalyst for methanation because of its low cost, highest activity, and highest selectivity for methane formation [4–6,8,9]. CO_2 methanation can demonstrate almost 100% methane selectivity when Ni-based catalysts are utilized. Al_2O_3, CeO_2, TiO_2, MgO, SiO_2, zeolite, and ZrO_2 are the most preferred Ni-based catalysts used for methanation [5,8,10–12]. $Ni-ZrO_2$ is an active Ni-based catalyst for CO_2 methanation as a result of enhanced Ni dispersion resulting from the presence of Zr. In all cases, a catalyst is required that is capable of increasing reaction rates within the temperature range of 25 to 500 °C and when the feed gas is composed of a 1:4 ratio of CO_2 and H_2 gas [13].

To avoid a thermodynamic barrier of the reaction and catalyst degradation, temperature control is required as a result of the extreme exothermic behavior of the reaction [14]. Thus, reactor temperature control is required to prevent thermodynamic limitation and catalyst sintering. A higher conversion rate to methane results from such control. An adiabatic, fixed-bed reactor in which the reactor is packed with some catalysts is the most common reactor used for catalytic methanation systems. Catalytic methanation is possible at low temperatures only with Ni-based catalysts. Low methane generation and catalyst sintering can occur at higher temperatures, whereas high pressure favors the catalytic methanation [15].

An instantaneous solar to hydrogen (STH) conversion efficiency of 24.4% has been achieved previously. Such conversion was carried out on CPV cells connected with EC cells. The system set the world efficiency record in outdoor test operations at the University of Miyazaki, Japan [16]. Subsequently, a highly efficient solar to hydrogen conversion system with a DC/DC converter was introduced. The resulting system had improved flexibility for variable radiation conditions [17]. We expanded the system from CPV cells to CPV modules and performed the operation outdoors at the University of Miyazaki, Japan. The system achieved highly efficient solar to hydrogen conversion under variable climatic conditions. The sunlight was collected using the highly efficient CPV modules with InGaP/InGaAs/Ge triple junction solar cells operating with DC/DC converters. The latter was operated as per the maximum power point tracking (MPPT) method. The power to gas (P2G) conversion system was analyzed using the PEM electrolysis method for solar to hydrogen conversion. The highest one-day STH efficiency of 18.78% for a subkilowatt-scale photovoltaic (PV) system using highly efficient CPV modules was successfully obtained under outdoor operation [18].

In this study, we discuss the outdoor operation of a solar to methane system. The electrical energy was supplied to EC cells and collected by highly efficient CPV modules under outdoor operation, and H_2 generated from solar energy was utilized in this methanation system. The reaction was performed within the reactors set up in the outdoor condition. Then, CH_4 was formed by reacting CO_2 and H_2 gases. Therefore, the solar-based methane could be utilized in the current infrastructure.

2. Experimental Procedure

Three highly efficient CPV modules (as shown in Figure 2a) were installed at the University of Miyazaki and connected in parallel with four sets of DC/DC converter EC cells (as shown in Figure 2b). Sunlight was converted to electricity by CPV modules and was supplied to EC cells. System performance is more than satisfactory on both sunny and cloudy days. This is a result of the efficient DC/DC converters connected to highly efficient CPV modules. For voltage matching between CPV modules and EC cells, DC/DC converters were used. Direct normal irradiance (DNI), which was input power in the system, was gauged by a pyrheliometer (EKO Instruments Co., Ltd., MS-56). The stored hydrogen energy was calculated by free energy of hydrogen ($\Delta G° = -237$ kJ/mol) and hydrogen generation rate (GR_{H2}), which was measured by a mass flow meter (MFM, Alicat Scientific M-2SLM-D-25COMP). Daily STH efficiencies of approximately 18% for sunny days and approximately 15% for cloudy days were achieved from this system [18]. The details of system configuration were shown in [18]. Disbanding of water molecules into H_2 and oxygen, and the subsequent addition of H_2 to CO_2, were attempted in the outdoor operation. The H_2 resulting from water splitting was subsequently reacted with CO_2 from the outside source.
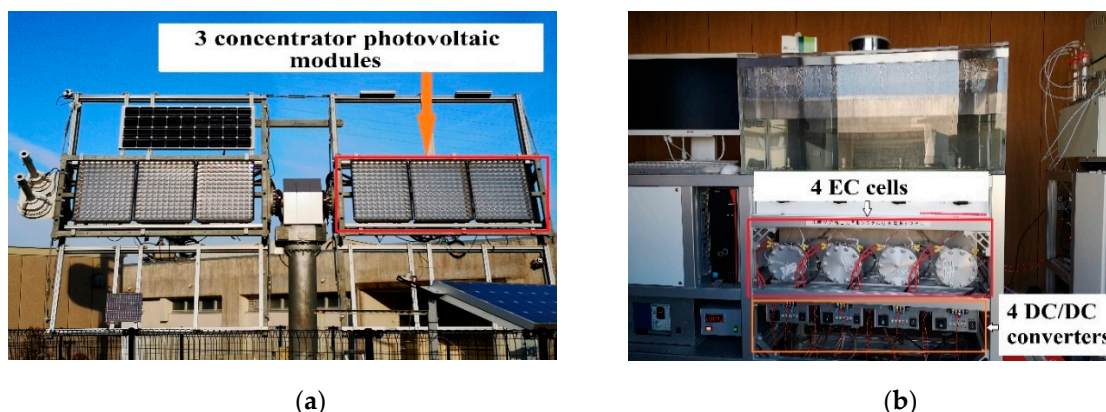
(a)

(b)

Figure 2. (**a**) View of the concentrator photovoltaics (CPV) outdoor configuration at the University of Miyazaki, Japan, and (**b**) view of 4 sets of DC/DC converters and electrochemical (EC) cells set up used for hydrogenation.

In the next step of the StM system, the Sabatier process, H_2 gas extracted from the electrolysis system was mixed with CO_2. The latter was introduced via a tank. The CO_2 hydrogenation or CO_2 reduction to CH_4 occurred within two reactors fed with Ni-based catalysts. Temperature is the next important parameter to achieve the highest CH_4 composition. Since the highest yield of CH_4 is obtained at a low temperature because of the exothermic nature of the reaction, the operating temperature must be below 300 °C [19]. Reverse-water, gas-shift reaction, and CO formation are favored when the temperature is above 500–800 °C [5,6]. To avoid catalyst deactivation due to sintering and carbon formation, the operating temperature should not exceed 500 °C [6,20]. Increasing temperature is an undesirable condition for CO_2 methanation because of the strongly exothermic reaction of CO_2. Higher pressures and lower temperatures are more favorable in thermodynamic methanation. At high temperatures, a high conversion can be maintained by increasing the pressures despite decreasing CH_4 generation and catalyst degradation. For lower-operating temperatures, an active catalyst is required, while the high-pressure operation is often uneconomical [21]. Since the methanation process is an extremely exothermic reaction, an effective method of temperature management is to cool the reactor inlet gas stream; this may cause undesired energy losses. Moreover, heat management in a fixed-bed reactor may be difficult, resulting in localized, hot spots. Use of an isothermal reaction in the fixed-bed reactor is an alternative cooling solution. In contrast, cooled reactors transfer the released heat from the reaction to a cooling medium. This may be difficult to manipulate within a single reactor. Therefore, at least two adiabatic reactors are needed to be connected in series for good control of reaction temperature in a fixed-bed reactor [9]. The design of the reactor is essential for thermal control of the system.

In our system, the reaction was carried out in two adiabatic fixed-bed reactors in which the Ni-based ZrO_2 catalyst bed was fixed as shown in Figure 3. The two reactors were connected in series to maximize the CH_4 generation. The external electricity was applied to heaters of reactors and the reactor temperatures were controlled by a proportional, integral, derivative (PID) controller without cooling systems. Gas/liquid separators were used to filter the byproduct H_2O to result in pure CH_4. The reaction performance was a function of the contact time of the reactant feed gas and the catalyst bed. If contact time is too short, decreased CH_4 concentrations will result. [22]. The size of the reactors is an important factor in determining the contact time between the feed gas and the catalyst. The outside diameter of each reactor was 19.05 mm, while the inside diameter was 16.57 mm, with a height of 200 mm for each. The produced H_2 from water electrolysis was directly applied to reactors after passing through gas/liquid separators and dryers. It was intended to feed pure H_2 to the methanation system without steam resulting from the water electrolysis, while CO_2 was introduced from the outside source. The flow rate of H_2 fed into the methanation system was measured by MFM, while that

of CO_2 was controlled by mass flow controller (MFC, Alicat Scientific MC-500SCCM-D-25COMP). The additional pressure into the reactors was not applied in our system.
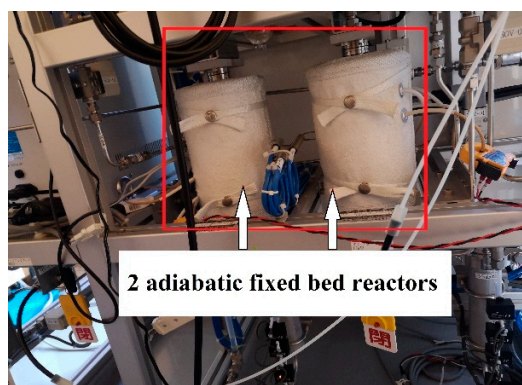

Figure 3. View of the two adiabatic fixed-bed reactors used for the methanation system.

Since the reactors were connected in series, most of the reaction developed within the first reactor (reactor 1). Simultaneously, the residual and unreacted gases (such as H_2 and CO_2) traveled from reactor 1 and maintained the reaction within the second reactor (reactor 2). Therefore, the output gas from reactor 2 was where system output was measured and analyzed. The composition of produced gases was quantitatively analyzed using a quadrupole mass spectrometer (QMS, MS 9600, Netzsch). No H_2O was observed in our system owing to the usage of filters and gas/liquid separators. The water was cooled and liquefied in the reactor after passing through the valves. The composition of methane was related to the feed mole ratio and feed temperature. Thus, the amount of CH_4 composition was given by various feed temperatures and stoichiometric ratio. The volume of CH_4 gas was not directly measured. It was assumed that the volume of CH_4 gas corresponded to 1/4 times the fed H_2 gas volume and was multiplied with the CO_2 to CH_4 conversion efficiency.

3. Results

3.1. Optimization for Operation Condition of Reactors

This section outlines the method to determine the operating temperature of reactors that yields the highest conversion to CH_4 and consequently generates the highest CH_4 composition. The conversion and yield of CH_4 depend upon the operating temperature and the catalysts utilized. Moreover, catalyst deactivation, carbon, and coke formation are related to the high temperature operation of the reactors. The preferred operating temperature must not only ensure catalyst productivity but also hinder catalyst thermal deactivation. Ni-based ZrO_2 catalysts can perform higher CH_4 selectivity within the temperature range of 200–300 °C [12].

The performance of methanation at temperatures ranging from 240 to 300 °C was analyzed in this study. The temperature of the gases generated from the catalytic reaction were measured. Figure 4a indicates the quantity of CO_2 converted to CH_4 from both reactors. The CO_2 conversion to CH_4 was calculated as shown in Equation (1):

$$CO_2 \text{ conversion} = \frac{V_{CH_4}\text{output} \times 100\%}{V_{CH_4}\text{output} + V_{CO_2}\text{output}}, \tag{1}$$

where V_{CH4} output and V_{CO_2} output are the volumes of CH_4 and CO_2 analyzed by QMS. The maximum conversion of CO_2 to CH_4 was 97.6%, which was achieved at a temperature of 260 °C. CO formation and catalyst deactivation will increasingly occur at temperatures higher than 320 °C [23,24]. Therefore, a temperature of 260 °C was utilized in our system. The reaction towards CH_4 can be controlled by varying the stoichiometric ratio of the reaction. Increased CO_2 conversion and CH_4 yields occur

at the stoichiometric ratio of 1:4 depending upon the types of the catalyst used [13]. Additionally, carbon deposition and carbon monoxide formation also depend upon the stoichiometric ratio of the reaction. The formation of carbon was observed when a molar ratio of 1:4 for CO_2/H_2 was not maintained [15]. This carbon generation may affect the catalyst performance and deactivate the catalyst. Consequently, it was necessary to determine the stoichiometric ratio that yielded the highest CO_2 conversion without negatively impacting the system. The CO_2 conversion to CH_4 was analyzed by changing the flow rate of CO_2 via MFC. As shown in Figure 4b, 1:4 was the best stoichiometric ratio for our system, which yielded a CO_2 conversion efficiency of 97.6%. The reactor temperatures were 260 °C for each reactor. When the stoichiometric ratio was changed to 0.9:4, reactor performance, as measured by CH_4 concentration, was 91%; when it changed to 1.1:4, 89% of CO_2 conversion was yielded, i.e., an efficiency lower than that of 1:4.
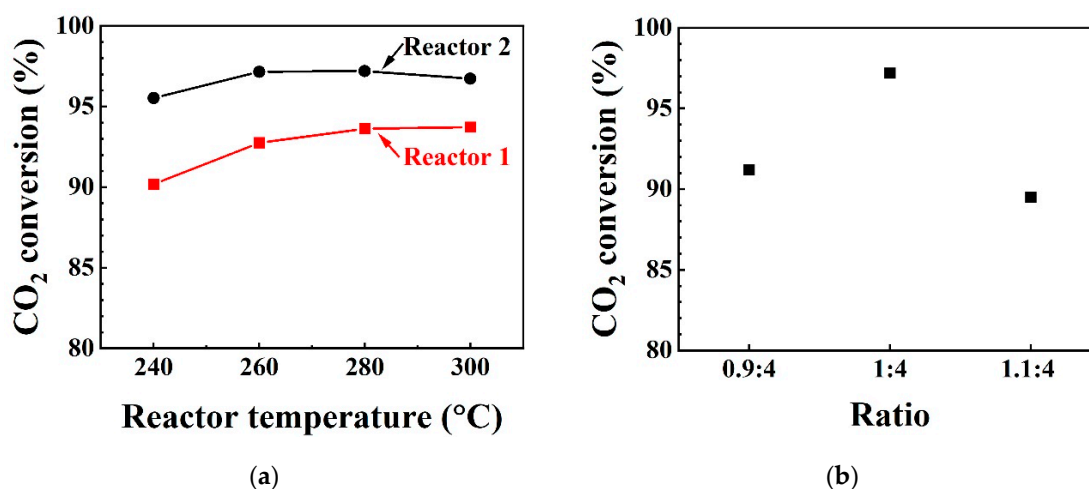

Figure 4. (**a**) Effect of reactor temperature on concentration of methane and (**b**) effect of ratio ($CO_2:H_2$) on CO_2 conversion to CH_4.

3.2. Measurement Result of the System under Outdoor Conditions

3.2.1. Validation of Methane Concentration during Outdoor Operation

Subsequent to determining the best feed ratio and reactor operating temperatures, the performance of methanation was examined. The methanation data to be analyzed were under operating conditions on a clear, sunny day between 10:00 a.m. and 2:00 p.m. The target reactor temperature for both reactors was 260 °C. Gases were collected and calibrated each hour.

Figure 5a shows GR_{H2} compared to DNI. Figure 5b shows the internal temperatures of the reactors compared to the concentration of CH_4. A CO_2 conversion efficiency of 97.6% was maintained for approximately 4 h. Although the operating temperature was set to 260 °C, the inner temperature of reactor 1 increased over 260 °C. The cooling system was not utilized in this system. Therefore, the heat was released during the reaction. However, the temperature of reactor 2 was stable at the operating temperature (260 °C). This was because of the low reaction rates in reactor 2. Most of the reaction was performed in reactor 1 and thus the temperature of reactor 1 was higher than that of reactor 2 as a result. The average GR_{H2} was 1.19 NL/min in the experimental period (10:00 a.m. to 2:00 p.m.). CO_2 gas applied to the methanation system, which corresponds to one-quarter times the fed H_2 gas, was 0.30 NL/min. The total mixture gas, which fed to the system, was 1.48 NL/min. Due to the changing DNI during the experimental period, the generated H_2 gas changed. Therefore, mixture gas fed to the system and space velocity also changed. The degradation of catalysis could not be seen in the experimental period.
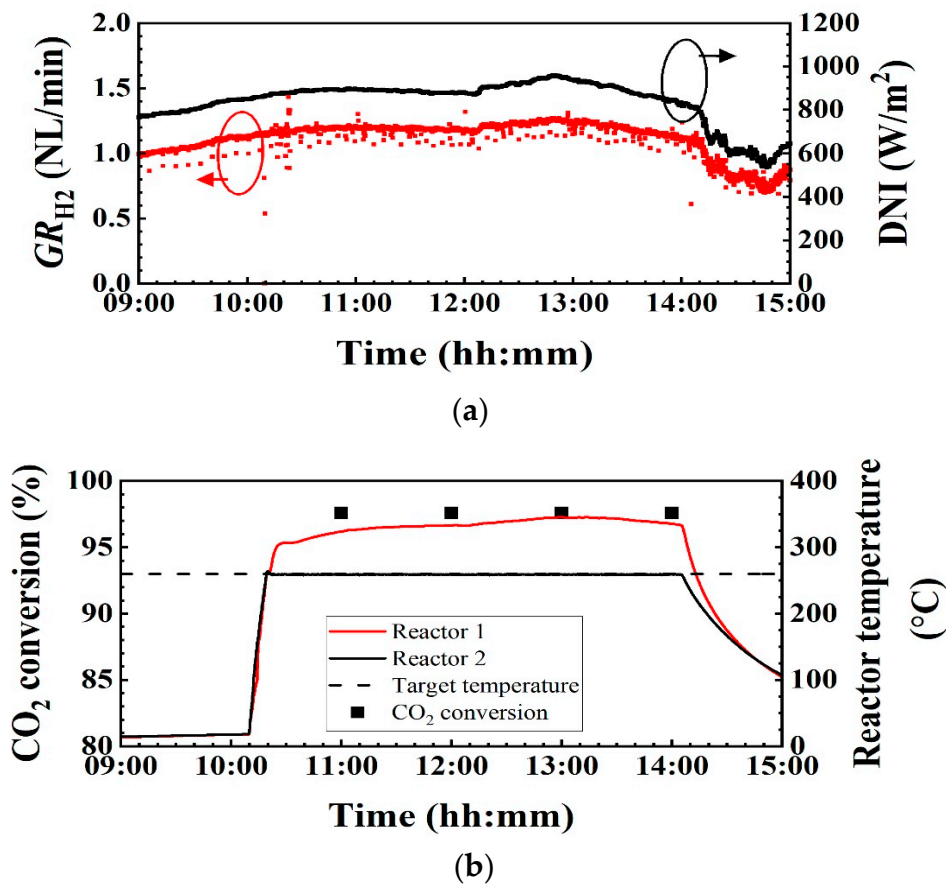
Figure 5. (**a**) Measured hydrogen generation rate (GR_{H2}) compared to direct normal irradiance (DNI) and (**b**) conversion of CO_2 to CH_4 compared to reactor temperature. Data in both plots were obtained on a clear, sunny day (15th November 2019).
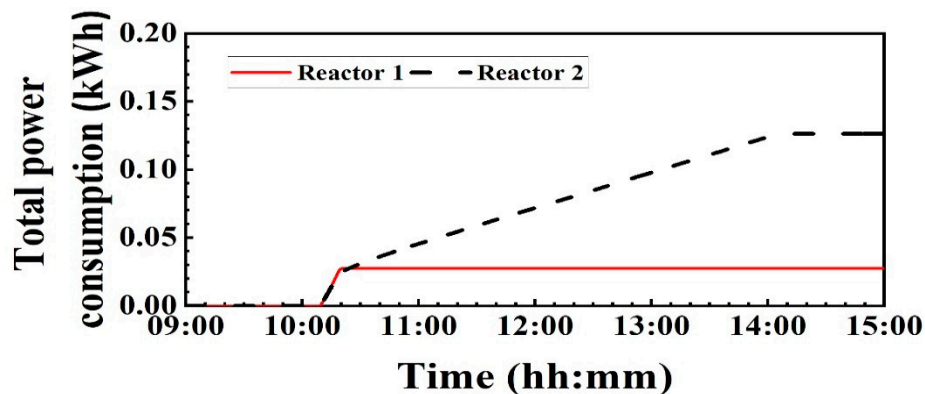
3.2.2. Power Consumption on the Methanation System

Thermocatalytic conversion of CH_4 is a highly exothermic reaction and consequently it may result in reactor overheating and low conversion of CO_2. Reactor cooling is critical to the methanation process to avoid catalyst deactivation. Operating temperature is the most critical parameter for optimizing the methanation system. Additional, critical operational factors such as catalyst deactivation, CO formation, CO_2 conversion, and CH_4 yield depend upon the operating temperature. The temperatures of the reactors should be maintained at a sufficiently high temperature to maintain catalytic reactions but also sufficiently low to avoid CO formation [25]. Heat management of the methanation system, specifically, reactor cooling and utilizing the reaction energy for external power to the reactors, is an active area of research in StM systems. The heat released from the reaction must be removed from the system and subsequently may be utilized in the electrolysis process [15,25]. Heat management is an important factor in reactor design. Optimization of heat removal, to ensure uniform temperatures within the reactors, is a currently unsolved concern. Cooled-packed reactor systems are a possible solution for heat management that is currently being investigated and is costly. The most known Sabatier reaction is shown below in Equation (2):

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \quad \Delta H^{\circ}_{298} = -164.9 \text{ kJ/mol} \tag{2}$$
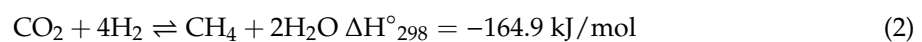
The reaction is significantly exothermic. The reaction consumes 4 moles of H_2 for each mole of CH_4 produced; 2 moles of H_2O are generated as a byproduct. Energy is required to initiate the reaction. Increasing reaction time provides some heat to perpetuate the reaction. The energy required to maintain the reaction decreases from the initial amount once the reaction becomes stable. Reactor temperature

was regulated by a proportional, integral, derivative (PID) controller. When reactor temperature increases because of the exothermic reaction, PID control switches regulate power depending upon reactor temperature. As a result, heat from the reactors provided the required reaction energy, and the power consumption of the methanation system was reduced. The total power consumption of the reactors was measured on a clear, sunny day from 10:00 a.m. to 2:00 p.m. local time. Figure 6a shows the reactor total power consumption compared with time. Although the reaction initiates in reactor 1, generated gases, residual, and unreacted gases, maintain the reaction in reactor 2. The reaction rate of reactor 2 was lower than that of reactor 1. Therefore, the total power consumption of reactor 2 was higher than that of reactor 1. It may be observed that after the initial energy was provided, the total power consumption of reactor 1 stabilizes as a result of the Sabatier effect. The heat of reaction for reactor 1 reduces power consumption of reactor 1, whereas for reactor 2, the reaction rate will be reduced because the majority of the reaction occurs in reactor 1. Therefore, more energy was consumed by reactor 2 to maintain the temperature and reaction. A total of 0.145 kWh was required for operation under sunny conditions. Figure 6b indicates the total power consumption of the reactors under overcast conditions. The DNI was negligible as was the generation of H_2. The reactors required more energy under cloudy conditions due to low reaction rates. The total power consumption of 0.281 kWh was observed under overcast conditions.
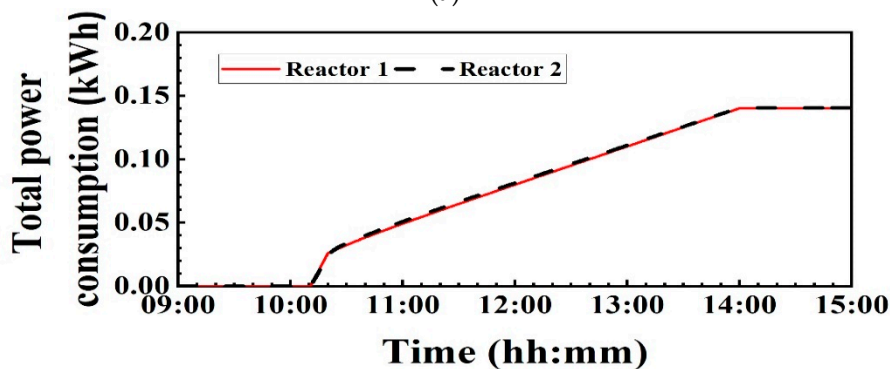
Figure 6. Total power consumption of the reactors under (**a**) a sunny conditions (15th November 2019) and (**b**) overcast conditions (6th December 2019).

4. Discussion

The methanation process is a strongly exothermic reaction and requires external energy to initiate the reaction. Subsequent to initiation, the reaction can be maintained by the heat released. As a result, the energy requirements for the methanation system decrease significantly after reaction initiation. Energy consumption of the methanation system is a significant issue for the efficient conversion of solar

energy to gas. It is important to note that a highly efficient StM system is a result of highly efficient CPV modules, highly powerful DC/DC converters, and highly active catalysts. The StM conversion system performed well and achieved high efficiency under variable weather conditions. This was a result of efficient CPV modules and active catalysts.

Utilizing methanation, StM is a chemical energy storage technique where renewable energy is stored as gas for later use in a gas grid infrastructure. The photocatalytic conversion of CO_2 and H_2 into artificial CH_4 might be a useful approach with applications in transportation and the current gas grid infrastructure. Potentially, CH_4 could be stored safely and distributed widely as natural gas in the future. The StM method could be utilized to produce CH_4 as a renewable energy.

The stored chemical energy of CH_4 should be considered in StM conversions because it is directly used in power generation via combustion. Figure 7 shows a schematic illustration of combustion energy of CH_4. CH_4 has a combustion energy of −802 kJ/mol. Solar to methane efficiency (η_{StM}) is defined as shown in Equation (3):

$$\eta_{StM} = \frac{\text{Combustion energy of produced methane} \times \text{Moles of produced methane}}{\text{Input energy} + \text{Electrical energy required to heat reactors}},$$
$$= \frac{|\Delta H°| \times \text{amount of CH}_4}{E_{DNI} + E_{reactors}}, \tag{3}$$

where the stored chemical energy of produced methane yields the combustion energy ($\Delta H° = -802$ kJ/mol). The integrated irradiance is denoted as E_{DNI}, while the term $E_{reactors}$ represents the energy consumed by the reactors in the methanation system.
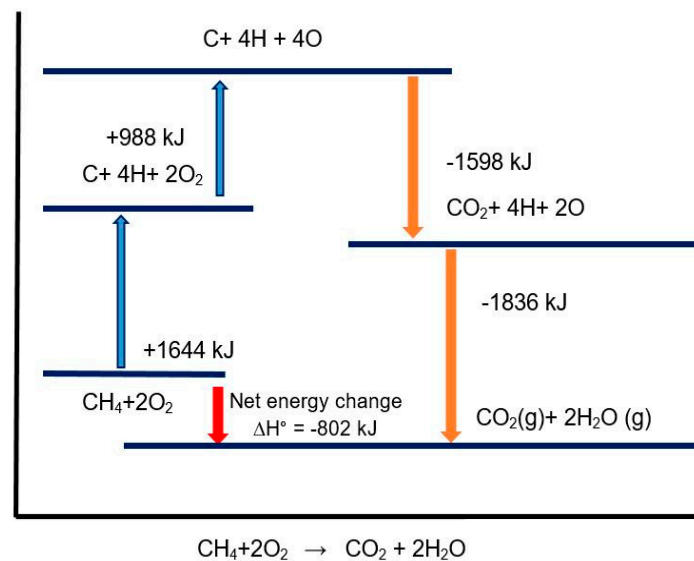

Figure 7. Schematic illustration of the combustion energy contained in methane.

Table 1 shows the summary of power input and output for our system. The CH_4 generation rate was calculated based on mole fractions and generation rate of H_2 input into the reaction. The calculation assumes that the CH_4 generation rate corresponds to one-quarter times the input of H_2. Subsequently, the CH_4 generation rate was multiplied with the calculated conversion of CO_2 to CH_4 (97.6%). The rate of H_2 input into the StM system was evaluated by MFM. The conversion of CO_2 to CH_4 was analyzed and assessed by QMS. For sunny conditions (on 15th November 2019), an efficiency of 13.8% was achieved as shown in Table 1. In contrast, the system could not generate electricity from CPV modules under an overcast condition because the CPV modules use only the direct-beam component. Therefore, the hydrogen generation and Sabatier process did not operate under an overcast condition.

Table 1. Summary of power input and output for the methanation system and conversion efficiency of solar energy to methane for sunny conditions (on 15th November 2019).

Input Energies		Produced Gases (Output)			
E_{DNI} (kWh)	$E_{reactors}$ (kWh)	Amount of H_2 during Experimental Period (mol)	Amount of CH_4 during Experimental Period (mol)	Stored Energy of Produced Methane (kWh)	η_{StM}
4.584	0.145	11.985	2.924	0.651	0.138 (13.8%)

Table 2 shows the one-day elemental efficiencies focused on solar to hydrogen conversion. The elementary efficiencies are defined as follows: η_{CPV} is the CPV module efficiency; η_{DCDC} is the conversion efficiency of the DC/DC converters; η_{EC} is the energy conversion efficiency from DC electricity into the free energy of hydrogen at the electrolyzer [18]. Especially, η_{EC} decreased in comparison with previous work [18]. The system in this study had consisted of three CPV modules and operated at the high operating current of the electrolyzer, which leads to reduce η_{EC}. The CO_2 conversion to CH_4 after passing thought reactors 1 and 2 was 97.6% as shown in Figure 5b. The StM efficiency could be improved by optimization of system configuration such as the number of CPV modules and operating current of the electrolyzer. while considering space velocity.

Table 2. One-day elemental efficiencies on the system.

	η_{CPV}	η_{DCDC}	η_{EC}
Sunny day 15th November 2019	27.4%	89.3%	70.2%

5. Conclusions

Effective storage of solar energy is required because solar energy production is variable and depends on solar irradiance and weather conditions. The conversion of the StM system is proposed as a long-term method of solar energy storage. In a StM system, the hydrogenation of CO_2 was accomplished by utilizing the hydrogen extracted form solar power. An efficient StM system was operated outdoors during a field test at the University of Miyazaki, Japan. The StM system consisted of highly efficient CPV modules, DC/DC converter electrolyzer sets, directly applying hydrogen to the methanation system, and two adiabatic fixed-bed reactors with Ni-based catalysts. The CO_2 conversion to CH_4 was affected by reactor temperatures and the ratio of H_2 and CO_2. The inner temperature of reactor 1 (first reactor) increased over the operating temperature (260 °C) due to the exothermic reaction of CH_4 conversion. The StM's performance was analyzed and it was found that the highest conversion of CO_2 to CH_4 (97.6%) was observed at a reactor temperature of 260 °C and the stoichiometric ratio of H_2 and CO_2. This indicated that CO_2 hydrogenation reaction was favored at relatively low temperatures. Then, the total power consumption of the reactors was analyzed for the sunny and overcast conditions. A conversion efficiency 13.8% for solar to methane on a clear sunny day was obtained in our system. Natural gas composition often contains at least 80% of CH_4. Since our generated gas composition contained more than 80% of CH_4, the practical impact of our efficient StM system is significant. It is essential to optimize the system configuration and to increase the StM efficiency for reducing the production cost of CH_4 using the methanation system.

References

1. Jia, J.; Seitz, L.C.; Benck, J.D.; Huo, Y.; Chen, Y.; Ng, J.W.D.; Bilir, T.; Harris, J.S.; Jaramillo, T.F. Solar water splitting by photovoltaic-electrolysis with a solar to hydrogen efficiency over 30%. *Nat. Comm.* **2016**, *7*, 13237. [CrossRef] [PubMed]

2. Brethome, F.M.; Williams, N.J.; Seipp, C.A.; Kidder, M.K. Direct air capture of CO_2 via aqueous-phase absorption and crystalline-phase release using concentrated solar power. *Nat. Energy* **2018**, *3*, 553–559. [CrossRef]

3. Carmo, M.; Fritz, D.L.; Mergel, J.; Stolten, D. A comprehensive review on PEM water electrolysis. *Int. J. Hydrogen. Energy* **2013**, *38*, 4901–4934. [CrossRef]

4. Gotz, M.; Lefebvre, J.; Mors, F.; McDaniel, K.; Graf, F.; Bajohr, S.; Reimert, R.; Kolb, T. Renewable power-to-gas: A technological and economic review. *Renew. Energy* **2016**, *85*, 1371–1390. [CrossRef]

5. Wieclaw-Solny, L.; Wilk, A.; Chwola, T.; Krotki, A.; Tatarczuk, A.; Zdeb, J. Catalytic carbon dioxide hydrogenation as a prospective method for energy storage and utilization of captured CO_2. *J. Power Technol.* **2016**, *96*, 213–218.

6. Stageland, K.; Kalai, D.; Li, H.; Yu, Z. CO_2 methanation: The effect of catalysts and reaction conditions. *Energy Procedia* **2017**, *105*, 2022–2027. [CrossRef]

7. Wei, W.; Jinlong, G. Methanation of carbon dioxide: An overview. *Front. Chem. Sci. Eng.* **2011**, *5*, 2–10. [CrossRef]

8. Marinoiu, A.; Cobzaru, C.; Raceanu, M.; Varlam, M.; Carcadea, E.; Cernatescu, C. Carbon dioxide conversion to methane over nickel base catalyst. *Rev. Roum. Chim.* **2015**, *60*, 249–256.

9. Schaaf, T.; Grunig, J.; Schuster, M.R.; Rothenfluth, T.; Orth, A. Methanation of CO_2-storage of renewable energy in a gas distribution system. *Energy Sustain. Soc.* **2014**, *4*, 1–14. [CrossRef]

10. Da Silva, D.C.; Letichevsky, S.; Borges, L.E.; Appel, L.G. The Ni/ZrO_2 catalyst and methanation of CO and CO_2. *Int. J. Hydrogen Energy* **2012**, *37*, 8923–8928. [CrossRef]

11. Takano, H.; Kirihata, Y.; Izumiya, K.; Kumagai, N.; Habazaki, H.; Hashimoto, K. Highly active Ni/Y-doped ZrO_2 catalysts for CO_2 methanation. *Appl. Surf. Sci.* **2016**, *388*, 653–663. [CrossRef]

12. Takano, H.; Shinomiya, H.; Izumiya, K.; Kumagai, N.; Habazaki, H.; Hashimoto, K. CO_2 methanation of Ni catalysts supported on tetragonal ZrO_2 doped with Ca_{2+} and Ni_{2+} ions. *Int. J. Hydrogen Energy* **2015**, *40*, 8347–8355. [CrossRef]

13. Barbarossa, V.; Vanga, G. Methanation of carbon dioxide. In Proceedings of the XXXIV Conference Meeting of the Italian Section of the Combustion Institute, Roma, Italy, 24–26 October 2011.

14. Bengaouer, A.; Ducamp, J.; Champon, I.; Try, R. Performance evaluation of fixed-bed, millistructured, and metallic foam reactor channels for CO_2 methanation. *Can. J. Chem. Eng.* **2018**, *96*, 1937–1945. [CrossRef]

15. Mendoza-Hernanda, O.S.; Shima, A.; Matsumoto, H.; Inoue, M.; Abe, T.; Matsuzaki, Y.; Sone, Y. Exergy valorization of a water electrolyzer and CO_2 hydrogenation tandem system for hydrogen and methane production. *Sci. Rep.* **2019**, *9*, 6470. [CrossRef] [PubMed]

16. Nakamura, A.; Ota, Y.; Koike, K.; Hidaka, Y.; Nishioka, K.; Sugiyama, M.; Fuji, K. A 24.4% solar to hydrogen energy conversion efficiency by combining concentrator photovoltaic modules and electrochemical cells. *Appl. Phys. Express* **2015**, *8*, 107101. [CrossRef]

17. Yamashita, D.; Nakao, H.; Yonezawa, Y.; Nakashima, Y.; Ota, Y.; Nishioka, K. A new solar to hydrogen conversion system with high efficiency and flexibility. In Proceedings of the IEEE 6th International Conference on Renewable Energy Research and Applications ICRERA, San Diego, CA, USA, 5–8 November 2017; pp. 441–446.

18. Ota, Y.; Yamashita, D.; Nakao, H.; Yonezawa, Y.; Nakashima, Y.; Ebe, H.; Inagaki, M.; Mikami, R.; Abiko, Y.; Iwasaki, T.; et al. Highly efficient 470W solar-to-hydrogen conversion system based on concentrator photovoltaic modules with dynamic control of operating point. *Appl. Phys. Express* **2018**, *11*, 077101. [CrossRef]

19. Schlereth, D.; Hinrichsen, O. A fixed-bed reactor modeling study on the methanation of CO_2. *Chem. Eng. Res. Des.* **2014**, *92*, 702–712. [CrossRef]

20. Gotz, M.; Koch, A.M.; Graf, F. State of the art and prospective of CO_2 methanation process concepts for power-to-gas applications. In Proceedings of the International Gas Union Research Conference, Copenhagen, Denmark, 17–19 September 2014.

21. Ghaib, K.; Ben-Fares, F.Z. Power-to-methane: A state-of-the-art review. *Renew. Sust. Energy Rev.* **2018**, *81*, 433–446. [CrossRef]

22. Yingli, W.; Jiao, L.; Qiang, L.; Jian, Y.; Fabing, S. Performance comparison of syngas methanation on fluidized and fixed bed reactors. In Proceedings of the 13th International Conference on Fluidization New Paradigm in Fluidization Engineering, Gyeong-ju, Korea, 16–21 May 2010; p. 102.

23. Ashok, J.; Ang, M.L.; Kawi, S. Enhanced activity of CO_2 methanation over Ni/CeO_2-ZrO_2 catalyst: Influence of preparation methods. *Catal. Today* **2017**, *281*, 304–311. [CrossRef]

24. Zhen, W.; Li, B.; Lu, G.; Ma, J. Enhancing catalytic activity and stability for CO_2 methanation on Ni@MOF-5 via control of active species dispersion. *Chem. Comm.* **2015**, *51*, 1728–1731. [CrossRef]

25. Sun, D.; Simakov, D.S.A. Thermal management of a Sabatier reactor for CO_2 conversion into CH_4: Simulation-based analysis. *J. CO_2 Util.* **2017**, *21*, 368–382. [CrossRef]