

MOLTEN-SALT TUBULAR ABSORBER/REFORMER (MoSTAR) PROJECT: REFORMING PERFORMANCE OF REACTOR TUBES DURING INTERMITTENT HEATING

Nobuyuki Gokon

Center for Transdisciplinary Research, Niigata
University, 8050 Ikarashi 2-nocho, Nishi-ku,
Niigata 950-2181, JAPAN

Shingo Yamashita

Department of Chemistry & Chemical
Engineering, Faculty of Engineering, Niigata
University 8050 Ikarashi 2-nocho,
Nishi-ku, Niigata 950-2181, JAPAN

Taebeom Seo

Department of Mechanical Engineering, Inha
University, #253, Yanghyundong, Namgu,
Incheon, 402-751 Korea

Tatsuya Kodama

Department of Chemistry & Chemical
Engineering,
Faculty of Engineering, Niigata University
8050 Ikarashi 2-nocho,
Nishi-ku, Niigata 950-2181, JAPAN

Tsuyoshi Hatamachi

Department of Chemistry & Chemical
Engineering, Faculty of Engineering, Niigata
University 8050 Ikarashi 2-nocho,
Nishi-ku, Niigata 950-2181, JAPAN

ABSTRACT

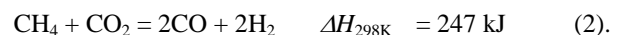
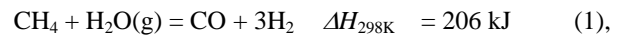
Reforming performances for the double-walled reactor tubes with $\text{Na}_2\text{CO}_3/\text{MgO}$ composite thermal storage was examined by an intermittent heating. The intermittent heating of the reactor tubes is composed of the heat-discharge (or cooling) mode and the subsequent heating mode. The heat-discharging mode simulates a fluctuating insolation for cloud passages. The heating mode simulates a heating of reactor due to concentrated solar radiation by using an electric furnace. The internal tube of the reactor was packed with the 2wt% Ru/ Al_2O_3 catalyst balls while the thermal storage materials were filled in the annular region of the reactor tubes. The reactor was heated up to 920°C in the cylindrical electric furnace and the CH_4/CO_2 mixture was fed into the internal catalyst tube at gas hourly space velocity (GHSV) of 12500 h^{-1} .

Through the cooling mode and the subsequent heating mode, temperature variations of reactor tubes, catalyst and composite material, H_2/CO ratio variations of effluent gas from the reactor, higher heating value (HHV) power of reformed gas were respectively examined for the double-walled reactor tubes and a single-wall reactor tube without the thermal storage.

INTRODUCTION

Steam and CO_2 reforming processes are both candidate processes for converting concentrated solar high-temperature

heat to chemical fuels since they are high-temperature, highly endothermic processes [1,2].



The above reactions theoretically can upgrade the calorific value of natural gas or methane feed by 22-28% if the process heat is supplied from concentrated solar radiation. Practically, these processes have been investigated and demonstrated as solar high-temperature thermochemical processes by some research groups worldwide for more than two decades. The solar-processed syngas can be stored and transported for a conventional gas turbine (GT), or a combined cycle (CC), in order to generate electricity with a high conversion efficiency (up to 55% in a modern, large CC). It can be also readily converted to easily transportable liquid fuels such as methanol and DME. The production of transportable solar methanol or DME is very important for remote countries from the sunbelt regions since it may enable solar energy transportation from the sunbelt to remote countries, such as Japan.

Concentrated solar radiation has some specific properties such as high density, heterogeneous distribution of thermal flux, and frequent thermal transients due to the fluctuating insolation. Thus, conventional reactors used for reforming

system are necessary to be modified for the solar reforming process. Some solar-specific reformers have been developed, such as a tubular reformer with an integrated heat exchanger [3], a directly-irradiated metal tubular reactor [4-9], a volumetric receiver-reactor [10-13] a fluid-wall aerosol flow reactor [14] and a directly-irradiated carbon particle reactor [15].

In the directly-irradiated metal tubular reformer, the concentrated solar radiation is directly absorbed by an exterior metallic wall of the reactor tube and then the catalyst bed inside the tube is indirectly heated [4-9]. The Commonwealth Science and Industrial Research Organization (CSIRO), Australia, ran a solar reforming program using a solar dish concentrator in 1997-2002 [9]. Two reformer designs were tested: a multi straight tube reformer consisting of six straight tubes connected in parallel and a single coiled reformer tube [9]. In 2004, CSIRO began a new program to commercialize the technology by building a single, small tower module of 500kW solar capacity that would demonstrate larger scale reforming [16-18].

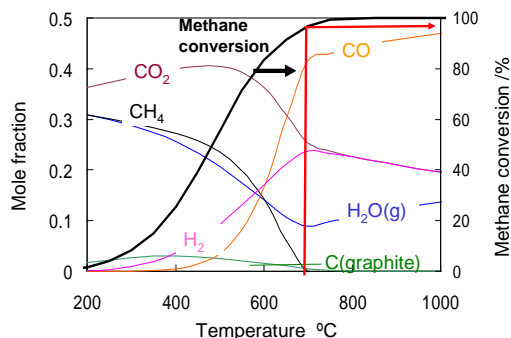


Figure. 1 chemical equilibrium composition and methane conversion in methane reforming in $\text{CH}_4 + 3\text{CO}_2$ system.

Solar tubular reformers have operated under a fluctuant incident solar radiation. However, catalytic methane reforming always requires a stable temperature operation even under intermittent insolation due to cloud passage. Figure 1 shows theoretical chemical equilibrium composition for CO_2 reforming of methane in $\text{CH}_4 + 3\text{CO}_2$ system. In addition, methane conversion is also plotted against temperature in this figure. Methane conversion X was estimated by the following equation:

$$X = \frac{y_{\text{CO}} + y_{\text{H}_2}}{4y_{\text{CH}_4} + y_{\text{CO}} + y_{\text{H}_2}} \quad (3)$$

where y_{CH_4} , y_{CO} , and y_{H_2} are the mole fractions of CH_4 , CO , and H_2 , respectively, in the effluent gas [19-22]. As seen in this figure, the methane conversion exceeds 90% at temperatures above 640°C [19-22]. Carbon is dominantly formed at temperature below 600°C, which frequently deactivates the catalyst [19-22]. Therefore, temperature of catalyst bed must need above 640°C under this reforming condition even during a cloud passage, otherwise methane feeding has to be interrupted.

The present authors (Niigata University, Japan) have proposed a tubular reformer system using novel “double-walled” reactor tubes with molten-salt thermal storage at high temperatures [19-23]. The reforming catalyst was filled into the internal tube of the double-walled reactor tube while the phase-change material (PCM) was filled as a thermal storage medium into the outer annular regions between the internal tube and the exterior solar absorber tube of the reactor tube. Because of the high heat capacity and large latent heat (heat of solidification) of the molten salt at high temperatures, the rapid temperature change of the reactor tubes can be circumvented under fluctuating insolation. The Molten-Salt Tubular Absorber/Reformer (MoSTAR) Project, a joint research project between Niigata University/Japan and Inha University/Korea, recently started in spring 2009. The objectives of MoSTAR project are to develop a novel-type of tubular absorber/reformer with molten-salt thermal storage at high temperature for use in solar natural-gas reforming or solar air receiver, and to demonstrate their performances on sun with a 5-kW_i dish-type solar concentrator at Inha University in Korea [24].

In this paper, reforming performances for the double-walled reactor tubes with $\text{Na}_2\text{CO}_3/\text{MgO}$ composite thermal storage was studied through the cooling (or heat-discharge) mode and the subsequent heating mode by using an electric furnace. The heat-discharging mode simulates a fluctuating incident solar radiation for a short term cloud passages. The heating mode simulates a re-heating of reactor by concentrated solar radiation after the cloud passage.

SOLAR REACTOR TUBES WITH MOLTEN SALT THERMAL STORAGE

Various shapes and designs of solar tubular reformers can be conceived. Examples of cavity-type reformers using solar directly irradiated reactor tubes [7,11,16,17] has been reported in our previous literatures[21].Some of them can be combined with solar dish concentrator. In an earlier paper, we tested a double-walled tubular reactor with molten-salt/MgO composite material for use as a solar directly irradiated reformer [19-23]. Figure 2 shows concept of solar reactor using the double-walled reactor tubes. For this type of reactor, where an internal catalyst tube is installed in the center of an exterior PCM tube, is to be used as a cavity-type reformer, solar heat must be conducted through the two container walls as well as a layer of relatively low-thermal-conductivity PCM to reach the catalyst and reactant gases in the internal tube during solar irradiation. Solar reforming is operated at a high temperature above 900°C by direct solar irradiation of the exterior PCM tube wall.

If cloud passage interrupts direct solar insolation only for short periods of time, this internal configuration of reactor will delay the cooling of internal catalyst bed due to heat supply from the PCM (cooling or heat-discharge mode)[20, 21]. When the reactor cools to below temperature of 680°C, the reactant gas must be stopped in order to prevent deactivation of catalyst due to coking. Subsequently, when the fully-cooled reactor reheats after long-term clouding (solar-heating mode), molten-

salt/MgO composite material may possibly conduct the irradiated solar heat to the internal catalyst tube sooner, than 100wt% molten-salt which is packed into the exterior tube of reactor. In a solar-heating mode, the reactor has never been evaluated.

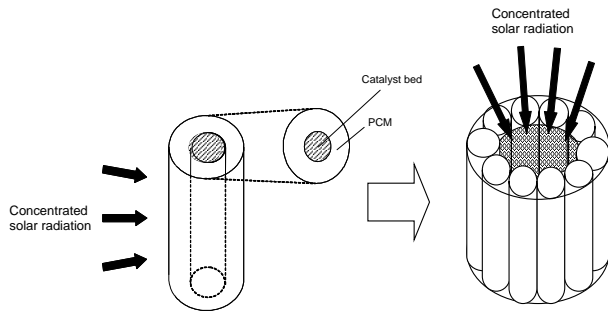


Figure. 2 Concept of solar reactor using the double-walled reactor tubes with molten salt/MgO composite material.

In the present study, the chemical reaction performances of the reactor tube were examined on CO₂ reforming of methane through cooling or heat-discharge mode and a subsequent heating mode at laboratory scale. Start-up time up to restart of reforming operation above 680°C, rates of methane conversion, variations of H₂/CO ratio in the reformed gas and power of reformed gas were evaluated.

EXPERIMENTAL PROCEDURE

Double-Walled Reactor Tubes. The tubes (length 356 mm) were fabricated from Inconel. The exterior PCM container tube dimensions were outer diameter 42.7 mm, inner diameter 37.1 mm, and thickness 2.8 mm. The internal catalyst tube dimensions were outer diameter 13.8 mm, inner diameter 9.8 mm, and thickness 2 mm. Composite material of Sodium carbonate (Na₂CO₂) and MgO was filled as a PCM material into the gap between internal and exterior tubes. 1450 and 1400 grams of Na₂CO₃/MgO were filled in the annular regions of the 90wt%Na₂CO₃/10wt%MgO and 80wt%Na₂CO₃/20wt%MgO, respectively. The composite material of Na₂CO₃ and MgO was pressed to form pellets, and the pellets were calcined at 950°C for 2 h in air. It appeared that a porous sintered ceramic network formed to some extent in the pellets of the composite material [21]. After calcination, the composite material was ground.

The powder of the composite material was filled into the annular region between interior and exterior tubes of the double-walled reactor; it was then densely packed by pressing and thumping using a metal stick. The reactor was placed vertically in an electric furnace and heated to 1000°C to develop a ceramic network in the composite [21]. After cooling to room temperature, the composite material in the annular region was pressed again to maximize the empty space in the upper part of the exterior tube. Powder of the composite

material was filled into this empty space and again densely packed by pressing and thumping. The reactor was again heated to 1000°C. These loading and heating processes were repeated several times to achieve a densely packed composite material in the exterior tube. Table 1 shows the total amounts and the storage capacities of thermal storage material packed in the exterior tube. The storage capacities were calculated in the range of 680-920°C. Their sensible heats for the Na₂CO₃ and MgO were calculated from the temperature dependence of the specific heat C_p [20].

Table 1 loading amount and storage capacity of composite materials.

Thermal storage	Loading amount / g	Storage capacity / kJ			Total storage capacity / kJ
		Sensible heat of Na ₂ CO ₃	Latent heat of Na ₂ CO ₃	Sensible heat of MgO	
90wt%Na ₂ CO ₃ * /10wt%MgO	1450	549	365	45	959
80wt%Na ₂ CO ₃ * /20wt%MgO	1400	471	314	86	871

*Phase change temperature of Na₂CO₃ is 858 °C [20,21].

Reforming Performance of the Reactor Tube during intermittent heating. Intermittent heating of the reactor tubes includes different two kinds of operation modes: 1) heating mode to simulate a direct heating of the reactor tubes by concentrated solar radiation; 2) heat-discharging mode to simulate solar reforming during cloud passages.

Figure 3 shows the experimental setup of the double-walled reactor tube for the reforming performance test. The internal tube of the reactor was packed with 2 wt% Ru-supported Al₂O₃ balls (25 g; diameter 3 mm; supplied by Sud-Chemie Catalysis Japan, Inc.), and a composite material was filled into the exterior tube of the reactor. The main body of the reactor tube was heated to 920°C by the electric furnace while CO₂ gas was passed into the internal catalyst bed. After reaching 920°C, a feed gas of CH₄/CO₂ mixture (molar ratio 1:3) was introduced into the internal catalyst tube (flow rate = 5 dm³min⁻¹; GHSV = 12,500 h⁻¹) at atmospheric pressure at room temperature. After the reforming reaction attained a steady state at 920°C, the cylindrical furnace powered off. The reactor was gradually cooled while passing the CH₄/CO₂ mixture for observation of variations in reforming performance during cooling (methane conversion versus cooling time). The periods of cooling varied every 10 min during 10-40 min. Temperatures (T_{rw} , T_{pcm} and T_{cat}) of the reactor tube were measured by K type thermocouples: T_{rw} , T_{pcm} and T_{cat} represents respectively temperature of reactor at exterior absorber wall, composite material and catalyst bed in the inner tube.

The heating mode of the reactor tube was performed as follows: after the reactor was cooled in 10-40 min, the reactor tube was again heated to 920°C under a constant power of the electric furnace while CH₄/CO₂ gas mixture continued to be always passed into the internal catalyst bed.

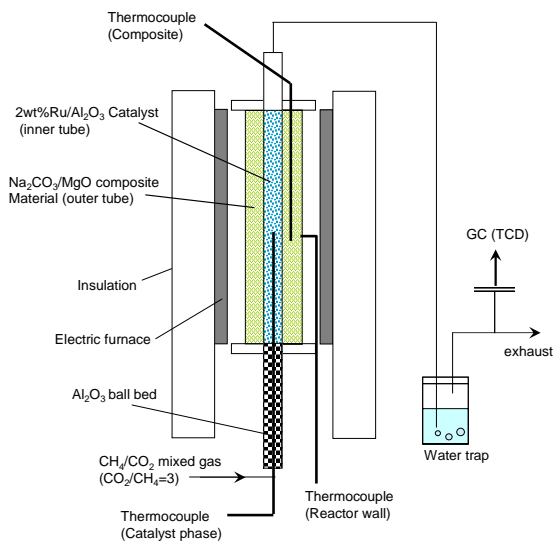


Fig. 3 Experimental setup of the reactor tube for a reforming performance test.

Effluent gases from the reactor were passed through a water trap to remove steam, then partially sampled and analyzed to determine gas composition by gas chromatography equipped with a thermal conductive detector (Shimadzu, GC-8A).

For comparison, a single tubular reactor without thermal storage, but with catalyst inside the tube, was tested under the same conditions.

RESULTS AND DISCUSSION

SEM observation and EPMA analysis for $\text{Na}_2\text{CO}_3/\text{MgO}$ composite material. The SEM micrograph of 90wt% Na_2CO_3 /10wt%MgO composite material before the high-temperature reaction is given in Fig. 4. A small portion of the 90wt% Na_2CO_3 /10wt%MgO composite material resembled a sponge-like ceramic brick. A porous sintered ceramic network, as expected, appears to have developed to some extent in the composite material. In addition, in the same visual field as that of the SEM micrograph, the chemical distribution of the composite material was analyzed and mapped for each element (Mg and Na) by using an electron-probe microanalyzer (EPMA), respectively. In the EPMA mapping, it appeared that Mg concentration was relatively lower in the position where Na concentration was higher. Particles with 5-10 μm size were locally formed and distributed in a matrix, and the particles were found to be MgO from the EPMA mapping for Mg element.

Reforming Performances of the Reactor during Cooling Mode. Table 1 shows the thermal storage capacities of the $\text{Na}_2\text{CO}_3/\text{MgO}$ composite materials packed in the annular region of the reactor. The capacity was calculated from the latent heat

of Na_2CO_3 and the sensible heat of Na_2CO_3 and MgO packed in the reactor, for a temperature change of 640-920°C. The capacity of the thermal storage media in the reactor reaches about 0.3 kWh in the present work.

Figure 5 shows time variations of the methane conversion and temperatures (T_{rw} and T_{cat}) of the single tubular reactor without thermal storage medium during the heat-discharge and subsequent heating modes. The residence time of the CH_4/CO_2 gas mixture was 0.36 s here. The fluctuating insolation by cloud passages was simulated by an intermittent power input to the electric furnace heating the double-walled reactor. After a temperature T_{cat} of the catalyst bed was stably held at 920°C, the electric furnace was powered off and cooling mode started. When a temperature T_{cat} was 920°C (Time = 0), a temperature T_{rw} was about 1000°C. After powering off the furnace, a temperature T_{cat} significantly dropped to 680 °C in 10 min, and the methane conversion decreased to around 95%. In the cooling times greater than 10 min, a temperature T_{cat} decreased to less than 680°C. As the results, methane conversion was rapidly dropped close to around 70% in 20 min, around 40% in 30 min and around 15% in 40 min. Thus, the reactant gas will be necessary to be stopped in order to prevent deactivation of catalyst.

These values of methane conversion and temperature T_{cat} described above were almost same with the minimum values of them at every cooling time. These results indicate that the single tubular reactor without thermal storage material sensitively responded for the intermittent heating from heat-discharging mode to heating mode. This characteristic of the reactor has an advantage for heating mode, but works as a negative factor due to rapid cooling of the reactor in the discharge mode.

For the double-walled reactor tubes with 80wt% Na_2CO_3 /20wt%MgO composite, time variations of the methane conversion and temperatures (T_{rw} , T_{pcm} and T_{cat}) of the reactor tubes are shown in Figure 6. After starting a cooling of the reactor tubes, temperatures T_{rw} , T_{pcm} and T_{cat} were respectively 1010, 1000 and 860°C in 10 min. Thus, methane conversion remained at 100%. In 20 min of cooling time, temperatures T_{rw} , T_{pcm} and T_{cat} decreased to 910, 910 and 790°C and methane conversion was 90%. As cooling time increases, temperatures T_{rw} , T_{pcm} and T_{cat} and methane conversion lowers. However, a dropping temperature was suppressed to $T_{\text{cat}} = 690$ °C in 40 min, and methane conversion of around 60 % was obtained in 40 min. Thus, obviously a use of the composite material contributes to suppression of dropping catalyst-temperature and methane conversion in comparison to the reactor without thermal storage material (Fig. 5).

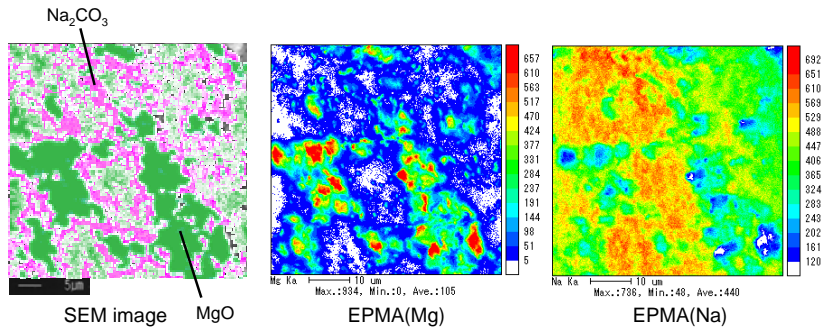


Fig. 4 SEM micrograph of 90wt%Na₂CO₃/10wt%MgO composite material and EPMA mappings for Mg and Na elements in the composite material.

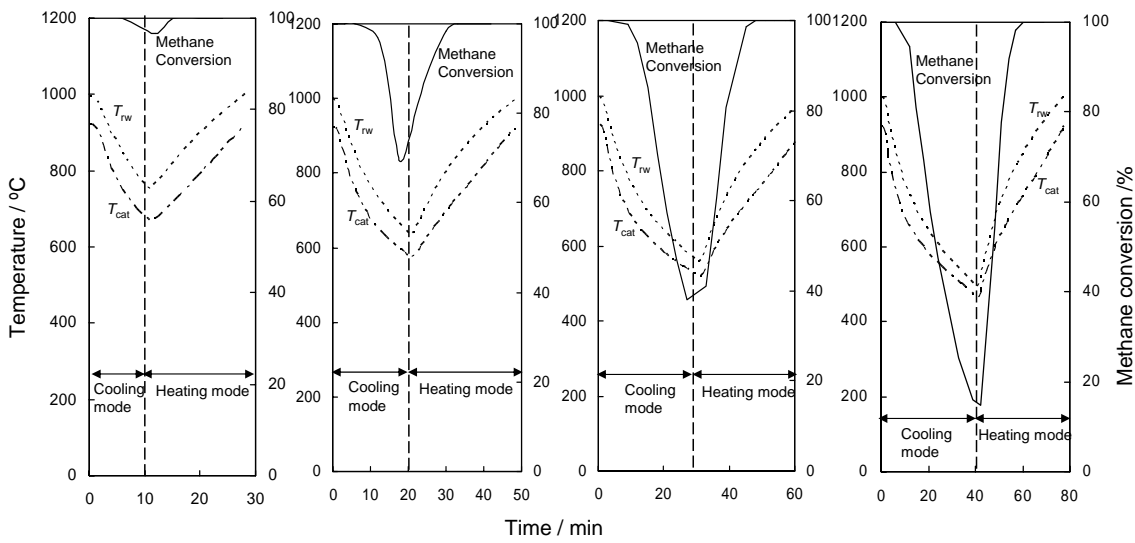


Fig. 5 time variations of the methane conversion and temperatures (T_{rw} and T_{cat}) of the inner catalyst tube during the heat-discharge (cooling) and subsequent heating modes. T_{rw} and T_{cat} indicates that temperatures of reactor wall and catalyst bed, respectively.

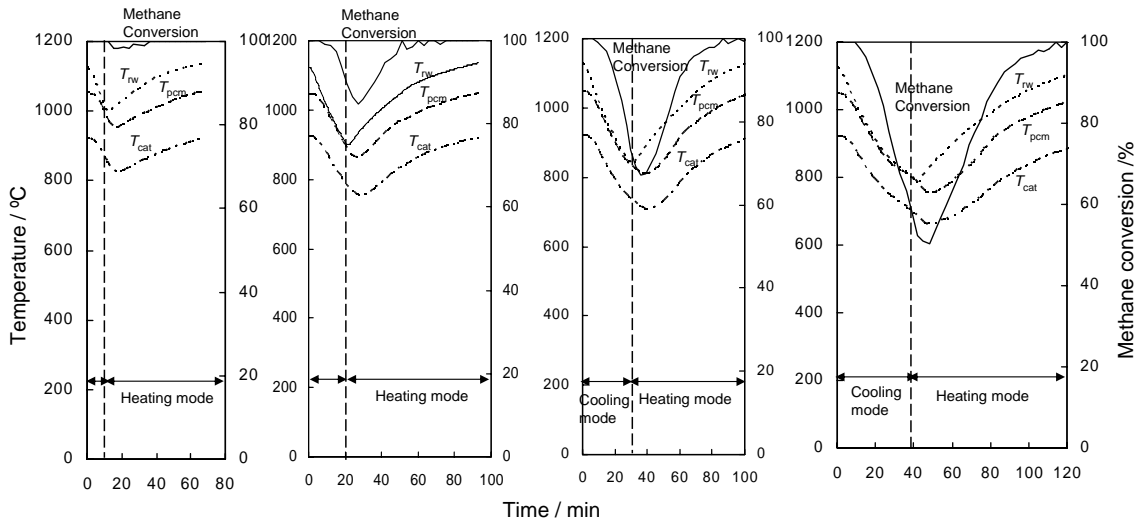


Fig. 6 time variations of the methane conversion and temperatures (T_{rw} , T_{pcm} and T_{cat}) of the reactor tube with 80wt%Na₂CO₃/20wt%MgO composite in their annular regions during the heat-discharge (cooling) and subsequent heating modes. T_{rw} , T_{pcm} and T_{cat} represents temperatures of reactor wall, PCM and catalyst bed, respectively.

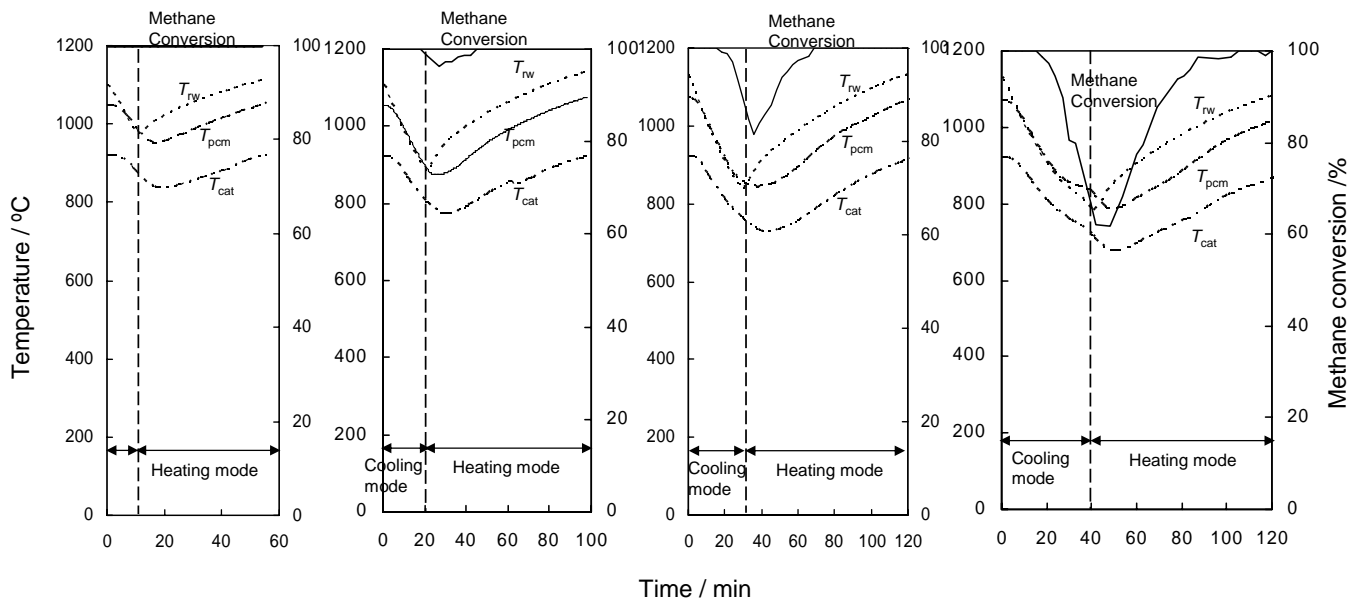


Fig. 7 Time variations of the methane conversion and temperatures (T_{fw} , T_{pcm} and T_{cat}) of the reactor tube with 90wt% Na_2CO_3 /10wt%MgO composite in their annular regions during the heat-discharge (cooling) and subsequent heating modes.

Figure 7 shows time variations of the methane conversion and temperatures of the reactor tube with 90wt% Na_2CO_3 /10wt%MgO composite during the heat-discharge and subsequent heating modes. After powering off the furnace, a temperature T_{cat} dropped to 880 °C in 10 min and 810°C in 20 min. A methane conversion of 100 % was hold until 20 min. In the cooling times of 30-40 min, a temperature T_{cat} was 760°C in 30 min and 720°C in 40 min. As the results, a methane conversion was around 90% in 30 min and around 70% in 40 min. These results for the 90wt% Na_2CO_3 /10wt%MgO composite indicate that higher temperature T_{cat} and greater methane conversion than those for the 80wt% Na_2CO_3 /20wt%MgO composite was sustained during the cooling time of 10-40 min after powering off the electric furnace.

In the case of the reactor with the thermal storage (Fig. 6 and 7), the values of methane conversion and temperature T_{cat} when heat-discharging mode of the reactor was changed into heating mode that were not identical to the minimum values of them at every cooling time. Namely, after the change of mode on the reactor, the catalyst-bed and the composite temperatures (T_{cat} and T_{pcm}) lowers ongoingly during several minutes, although a temperature of the exterior wall T_{fw} turns immediately to increase. The reason for the late response will come from a heat transfer through the cooled composite material from a rapidly-heated reactor wall toward an endothermic catalyst bed. This point is a disadvantage for the reactor with the composite material. However, it is expected that composite temperatures T_{pcm} increase in response to a thermal conductivity of the composite material. Thus, here, in order to evaluate the thermal response of the composite

material after the change of operation mode, we noticed the period of time that needed to return back until the high methane conversion of 90% from the time after re-starting to heat the reactor. For example, in the case of cooling time 30 min (Fig. 6 and 7), the period of time was 17 min for the 90wt% Na_2CO_3 /10wt%MgO composite and 29 min for the 80wt% Na_2CO_3 /20wt%MgO composite. The period of time was less for the 90wt% Na_2CO_3 /10wt%MgO composite than for the 80wt% Na_2CO_3 /20wt%MgO composite, although the 80wt% Na_2CO_3 /20wt%MgO composite had higher MgO than the 90wt% Na_2CO_3 /10wt%MgO composite. This means that the thermal response after the change of operation mode was better for the 90wt% Na_2CO_3 /10wt%MgO composite. Therefore, it is concluded that the 90wt% Na_2CO_3 /10wt%MgO composite shows apparently better performance for the both cooling and heating modes on the methane conversion.

H_2 /CO ratio in the reformed gas for the reactor tubes with and without thermal storage media were plotted against time during the heat-discharge and subsequent heating modes. The results were shown in Figure 9. The dotted line drawn in Fig. 9 represents time in which a heat-discharge mode of the reactor was changed into a heating mode of that. For the reactor tube without thermal storage medium, H_2 /CO ratio in the reformed gas was not stable and significantly fluctuated. However, in the case of the reactor tube with thermal storage media, H_2 /CO ratio remained at 0.5-0.6 with a slight fluctuation. Among the thermal storage media, a remarkable difference for stabilizing H_2 /CO ratio were not observed.

Figure 10 shows time variations of HHV power in the reformed gas during the heat-discharge and the subsequent heating modes. For the single tubular reactor without thermal

storage media, the HHV power was deeply dropped in the cooling times of 20-40 min. Thus, the reactant gas will be necessary to be stopped if a cloud passage continues to greater than 10 min. This constitutes barriers to a power generation in a fuel cell (SOFC), and methanol and hydrogen synthesis when reformed gas (H_2 and CO) is directly used without storage for availability. For the reactor tube with thermal storage media, a fluctuation of HHV power can be suppressed. If a cloud passage continues during around 20 min, the HHV power will stabilize with 10% variation. Among the tested thermal storage media, the 90wt% Na_2CO_3 /10wt%MgO composite can suppress a fluctuation of HHV power at a minimum.

However, a thermal storage layer of the reformer tubes creates temperature difference ($T_{rw} - T_{cat}$) between the solar absorbing surface and the catalyst bed. For the case of the reformer tube with the composite materials, as seen in Fig. 7 and 8, this difference was around 200°C through the heat discharge and heating modes. For the case of that without the annular storage layer, as seen in Fig.5, the difference was less than 100°C. With larger tubes this difference is expected to be even larger. Thus, a design of the reformer tube may be modified as a next step in order to improve a heat transfer. Figure 10 shows a design of a modified double-walled reformer tubes with a thermal storage layer. In Fig. 10, concentrated solar beam is directly irradiated to a partial region of an inner catalyst-packed tube of the double-walled reactor, while other area of the inner tube is surrounded by the thermal storage layer of the reactor. This new design of the reactor tube will

reduce a resistance created by the conduction through the reactor wall and a thermal storage layer in comparison to the present design of the double-walled reactor tubes.

CONCLUSIONS

Reforming performances for the double-walled reactor tubes with Na_2CO_3 /MgO composite thermal storage was examined for solar demonstration of the reformer tubes by an intermittent heating. The thermal storage capacity of 90wt% Na_2CO_3 /10wt%MgO composite material packed in the reactor tube was about 0.3 kWh. The reactor tube with the Na_2CO_3 /MgO composite could produce the reformed gas ($H_2 + CO$) at a 0.9 kW based on the HHV and at the methane conversion above 90 % for 20 min of the cooling or heat-discharge mode, and the HHV power of 0.75-0.9kW could be sustained with 10% fluctuation.

MoSTAR project is an international collaboration research between Niigata University in Japan and Inha University in Korea, and the development of molten-salt thermal storage media, the new design and the fabrication of absorber/reformer with the double-walled absorber tubes, and finally the solar demonstration are planned on the Inha University's 5-kW_t dish concentrator in Korea.

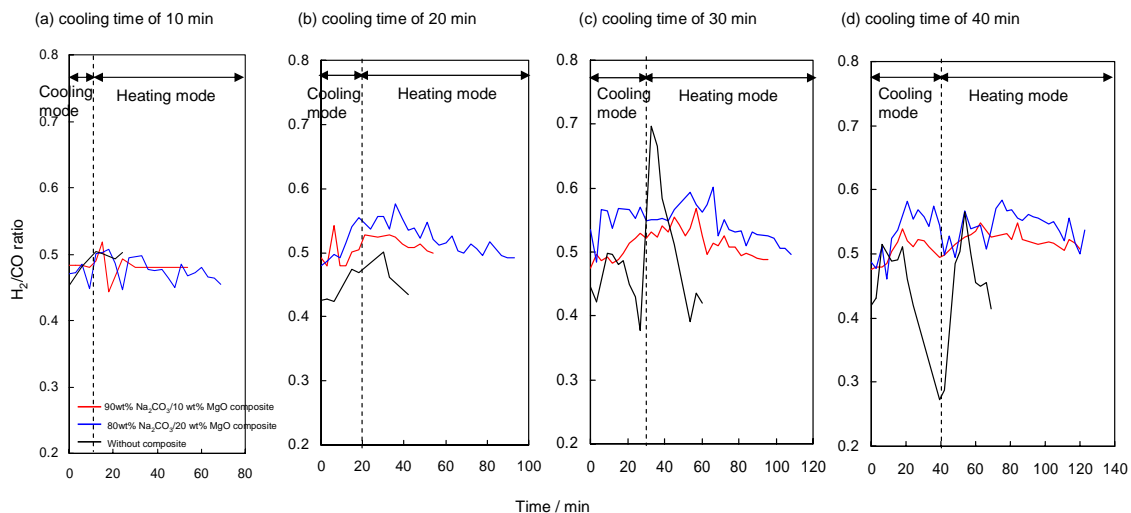


Fig. 8 Time variations of H_2/CO ratio in the reformed gas during the heat-discharge (cooling) and subsequent heating modes. The composition of the thermal storage media is shown in the figure.

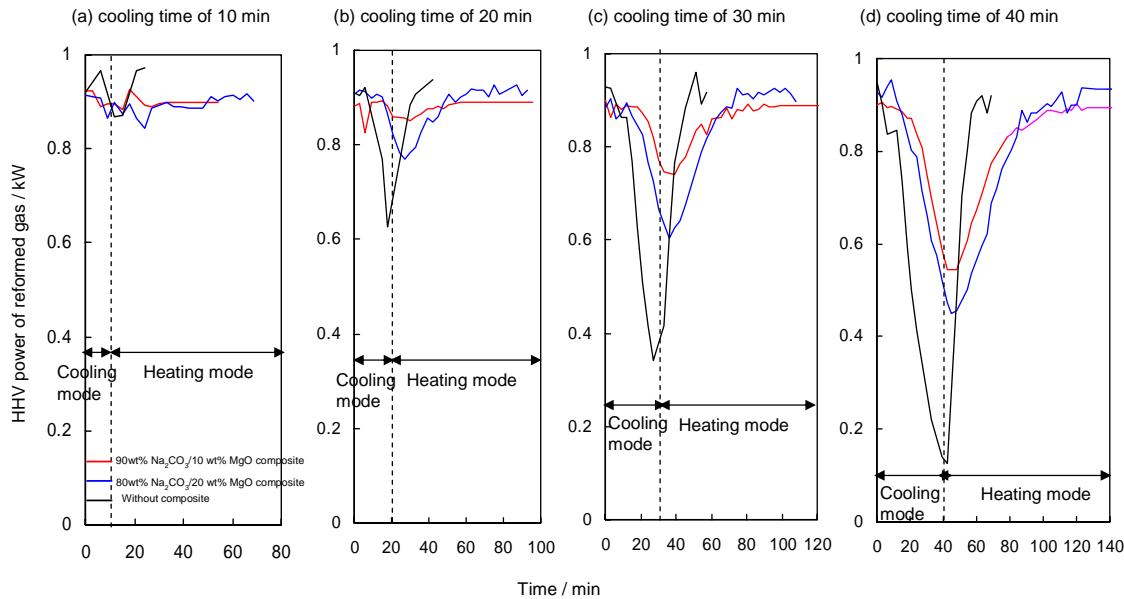


Fig. 9 Time variations of HHV power of the reformed gas during the heat-discharge (cooling) and subsequent heating modes. The composition of the thermal storage media is shown in the figure.

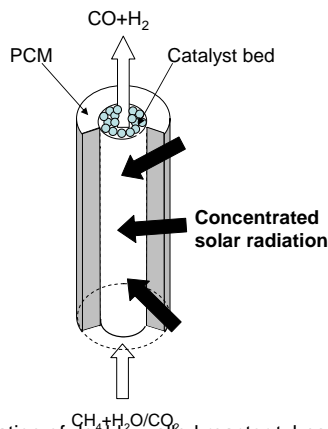


Fig. 10 Modification of double-walled reactor tubes with molten salt/MgO composite material.

NOMENCLATURE

- X Methane conversion (%)
 y_{CH_4} Mole fraction of CH_4 in the effluent gas (dimensionless)
 y_{CO} Mole fraction of CO in the effluent gas (dimensionless)
 y_{H_2} Mole fraction of H_2 in the effluent gas (dimensionless)
 T_{rw} Temperature of reactor at exterior absorber wall ($^{\circ}C$)
 T_{pcm} Temperature of composite material in the inner tube ($^{\circ}C$)
 T_{cat} Temperature of catalyst bed in the inner tube ($^{\circ}C$)

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