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SOLAR UPGRADE OF METHANE USING DRY REFORMING IN DIRECT CONTACT BUBBLE REACTOR

Khalid Al-Ali[1], Kodama S.[1], Kaneko H.[1], Sekiguchi H.[1], Tamaura Y.[1] and Chiesa M.[2]

[1] Department of Chemical Engineering, Tokyo Institute of Technology, Tokyo, Japan. Address: South Bldg 4, #401C, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan. Tel & Fax : +81-3-5734-2110. E-mail: kalali@masdar.ac.ae

[2] Laboratory for Energy and Nano-Science, Masdar Institute of Science and Technology, Abu Dhabi, UAE

Abstract

The reforming behavior of a direct contact bubbling CH_4-CO_2 mixture, was quantitatively investigated, in an alkali carbonate based molten salt system containing suspended Ni-Al_2O_3 catalyst. A thermodynamical process of a solar reformer of dry methane reforming was proposed to operate in a temperature range of 600-800°C. The selectivity of the thermal fluid have been validated according to specific requirements including lower melting point, thermal and chemical stability, acting simultaneously as heat transport and sensible heat storage. A ternary mixture of alkali carbonates system Na_2CO_3, K_2CO_3 and Li_2CO_3 of ratio 1:2:2 fulfills our requirements for the direct contact bubble reactor of the solar reformer, in which a CO_2-rich mixture of methane was reformed to produce synthesis gas. The reforming behavior was experimentally investigated to quantify the product compositions, pursuing to maximize the methane conversion and H_2 yield, while minimizing coke depositions and carbonization effects. Three types of Ni-loading (10%, 15% & 20 wt. %) - Al_2O_3 catalysts were prepared by impregnation using nickel nitrate solution. The results exhibited that 15%Ni-Al_2O_3 catalyst showed the highest activity and selectivity with respect to H_2 % yield (or H_2:CO production ratio) and carbon deposition rates. The thermodynamic analysis showed the positive effect of excess CO_2 on the process of dry CH_4 reforming in alkali carbonate salts; the higher CO_2/CH_4 ratio, the lower reaction temperature can be achieved; subsequently, minimizing the thermal decomposition of alkali carbonates. However, the experimental results expressed the increase of CO_2/CH_4 ratio in terms of higher methane conversion, whereas the H_2:CO production ratio was significantly decreasing, attributed to increase in water formation as a result of Reverse Water Gas Shift (RWGS) reaction. While, the carbon deposition is decreasing as per the theoretical results.

Keywords: Direct Contact Bubble Reactor, Solar Reformer, Methane Dry Reforming, Solar energy conversion, Methane Up-gradation

1. Introduction

The global directive into the development and utilization of the abundant solar energy, which results in no any or little pollution, is not only an urgent supplementary to the energy in the present stage, but also a foundation of energy structure in the future. It compels to deeply look at the efficient solar energy utilization and to examine the challenges and opportunities for the development of solar energy utilization as a competitive energy source. Solar fuels are part of the solution, they have the capacity to help satisfy the energy needs of the world without destroying it [1-2]

The conversion of solar energy into chemical energy carriers overcomes the main drawbacks of solar energy, namely: it low spatial density, its intermittent, and its inconvenient distribution [3]. Solar fuels, such as hydrogen, can be produced from upgrading fossil fuels. CO_2 reforming of natural gas (methane) is highly endothermic, catalytic process, which produces syngas (CO and H_2) [4].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^o_{@\,298K} = +247\ KJ/mol \tag{1}$$

Reaction enthalpy of the reformed product is larger than fuel source, hence heat output of fuel is enhanced. The challenge is to produce large amounts of chemical fuels directly from sunlight in robust, cost-effective ways while minimizing the adverse effects on the environment [1].

Solar reforming of methane is the most feasible technology due to both commercial and environmental reasons as; at relatively high temperature Solar Thermo-Chemical (STC) processes, the methane reforming reaction with CO_2 has a larger endothermic enthalpy per mole ΔH^o than that with H_2O, and it can be realized with STC energy conversion systems [5]. CO_2 reforming of methane would result in lower H_2/CO ratio in syngas, which is favorable to the synthesis of oxygenated compounds [6]. CO_2 Reforming process consumes two important greenhouse gases CO_2 and methane and converts them into valuable feedstock. Therefore it is of a great interest for environmental protection [7].

The main vector for this research will be the production of syngas from methane dry reforming, a potentially clean alternative to fossil fuels. Today, however, more than 90% of hydrogen is produced by using high temperature processes from fossil resources, mainly natural gas. If hydrogen is generated from solar energy, it is definitely a clean technology; no hazardous wastes or climate changing byproducts are formed.

Nevertheless, one of the essential problems in the solar reforming of methane is fluctuating incident solar radiation. The catalytic methane reforming with CO_2 requires stable operation under the fluctuation of insolation by a cloud passage. Moreover, the solar chemical receiver reactor to which the concentrated solar radiation is directed requires thermal uniformity inside the reactor [8]. One solution to these problems is to use the concept of Direct Contact Bubble Reactor (DCBR) with molten metal salt of highly heat capacity as heat transfer medium in the solar receiver-reactor. Here, we are proposing the importance of using direct heat transfer by utilizing the conceptual idea of DCBR for methane reforming with carbon dioxide.

Furthermore, due to the absence of any intervening wall separating the processing fluids, these units of DCBRs have many advantages over the traditional shell-and-tube heat exchanger, among which one can highlight higher thermal efficiency; greater simplicity of construction, that accordingly reducing capital, operating and maintenance costs; and the possibility of economically processing highly fouling and/or corrosive solutions.

DCBR is proposed to promote solar thermal energy storage idea with higher energy conversional capacity, higher thermal efficiency, more stable operation under the fluctuation of incident solar radiation and greater simplicity of construction

Despite the great advantages offered by DCBR, there are still many areas of uncertainty with respect to methane dry reforming processes with carbon dioxide, and these problems need to be solved before this application can be proceed commercially. The CH_4-CO_2 reforming reactions are highly endothermic that possess very high energy consumption. The current catalyst is not able to achieve conversion over 80% unless in extreme temperature conditions (> 800^oC). However, the objectives of this research are; to find out the catalytic thermal fluid which is suitable for the STC methane dry reforming for converting solar high-temperature heat to chemical fuels, to investigate the reforming behavior of CH_4 with CO_2 at lower temperature ranges $600 - 800^oC$, and to quantify the product compositions in the selected thermal fluid of alkali carbonate based molten salt system.

2. Experimental and Method

2.1. Experimental Set-up

The schematic diagram of the experimental system is shown in Fig.1. A narrow-bore cylindrical stainless steel reactor with body made of SUS-304 TP, 18 mm outer diameter, 1.5 mm thickness and 38 mm long, was used as the DCBR between the thermal fluid of alkali-metal carbonates molten salt system and the bubbling gas mixture of CH_4, CO_2 and the carrier gas, Ar.

An alkali-metal carbonate mixture of Na_2CO_3, K_2CO_3 and Li_2CO_3 of ratio 1:2:2, was used as a molten salt bath because it shows the lowest melting point, relatively close to eutectoid melting point, and has relatively high heat capacity value. The alkali-metal salt mixture was mixed with the Al_2O_3-supported Ni metal catalyst at a desired weight ratio. The selection of both thermal fluid and catalyst would be explained in details in next sections. A mixture of catalyst and molten salt was placed in the reactor.

A CH_4/CO_2 mixture of desired mole ratio was introduced through a narrow-bore stainless steel tube ($\emptyset_{inner} = 1mm$) to the bottom of the inside reactor. The flow rates of CH_4, CO_2 and inert gas Ar were controlled by mass flow meters. The total flow rate of the mixed gases feed ranged from 75 to 200 ml/min at atmospheric pressure.

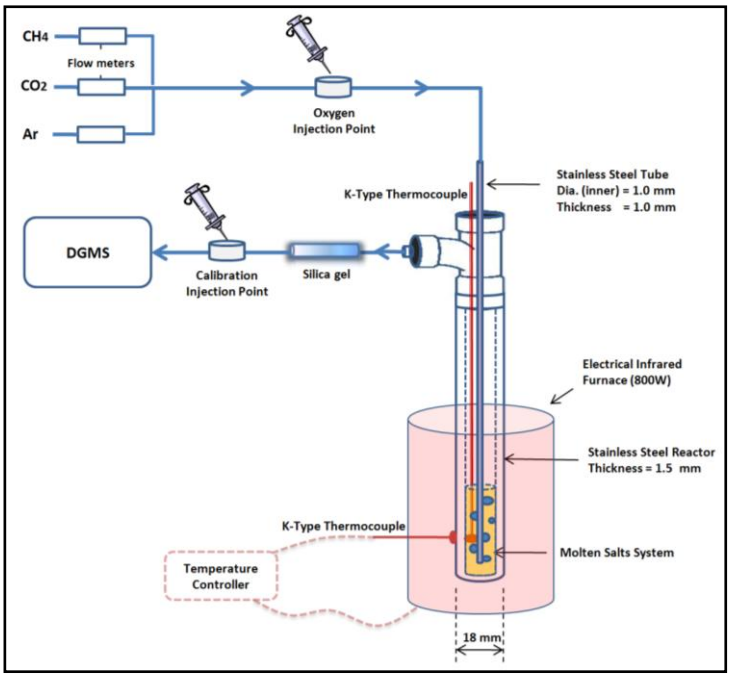


Fig. 1. Experimental apparatus for CO_2 reforming of methane in a molten salt DCBR

The reactor was externally heated by an infrared furnace of 0.8KW electrical power, 800 Volt and 8AMP up to $600 - 800^{o}C$ within $15 - 20$ min. Afterward, the CH_4/ CO_2 mixture was bubbled through the molten salt-catalyst mixed bath. The temperature was controlled using K-type thermocouple in contact with the external wall of the reactor, whereas, the inside K-type thermocouple in contact with the reactive bubbling system was used to record the real endothermic reaction temperature using software controlled thermal data acquisition system E830.

The effluent gases from the reactor were introduced to silica gel, to absorb the moisture content during the reaction. The dry effluent gases were analyzed using Direct Gas Mass Spectroscopy, DGMS (BRUKER-axs Model MS 9600 – Material Analysis and Characterization)

2.2. Selection of a Thermal Fluid

Alkali metal carbonate has been widely used in coal-CO_2 gasification [9] and the experimental results of Gokon et al, 2002 [5] showed that the methane reforming reaction with CO_2 using FeO catalyst in the molten carbonate is useful for the conversion of solar energy into chemical energy. AO Xian-quan and WANG H. [10] studied the reduction behavior of methane cracking in alkali-metal based molten salt system.

These suggest that the alkali molten carbonates mixture was one of promising molten salt for methane conversion and the most attractive thermal fluid to be applied to the solar thermochemical methane dry reforming for converting solar high-temperature heat to chemical fuels.

Mixed salts system is often used in molten salt system; the reason partly is mixed salts system generally has a low melting point, i.e. the melting points of pure salts of Li_2CO_3, Na_2CO_3 and K_2CO_3 are 618, 851 and 891, respectively. The melting point of ternary carbonate eutectic (32 wt% Li_2CO_3, 35 wt% K_2CO_3, and 33wt% Na_2CO_3) starts at $397^{o}C$ [11]. Moreover, the eutectic mixture of salts has a higher stability and to remain unchanged over a wide range of chemical conditions. This because coordination can be formed between anions and cations in molten salt mixture, and mixed molten salts system has higher coordination number if compared with its pure salt [10-11]

An experimental procedure have been proceeded to validate the results of mixed alkali-metal carbonates of KANTO Chemicals using Li_2CO_3, Na_2CO_3 and K_2CO_3 with purity of 99.95%, 99.97% and 99.95%, respectively. 21 data points have been decided on the ternary diagram, as shown in Fig.2. The ternary diagram boundaries' points (P1, P2, P3, P4, P6, P7, P10, P11, P15, P16, P17, P18, P19, P20, P21) have the values of binary mixed alkali-metal carbonates system using FACTSage Database Documentation of binary phase systems, 2009, whereas the ternary points of (P5, P8, P9, P12, P13, P14) are experimentally determined using simultaneous Thermogravimetric/Differential Thermal Analysis, TG/DTA, equipment.

The measured data of solidus and liquidus temperatures are summarized in Fig.2. The Eutectic melting point usually appears where the solidus and liquidus temperatures are coinciding. Accordingly, point P9, highlighted in Fig.2, with ternary mixture of alkali carbonates system Na_2CO_3, K_2CO_3 and Li_2CO_3 of ratio 1:2:2 reveals the closely rapprochement to the eutectic point.

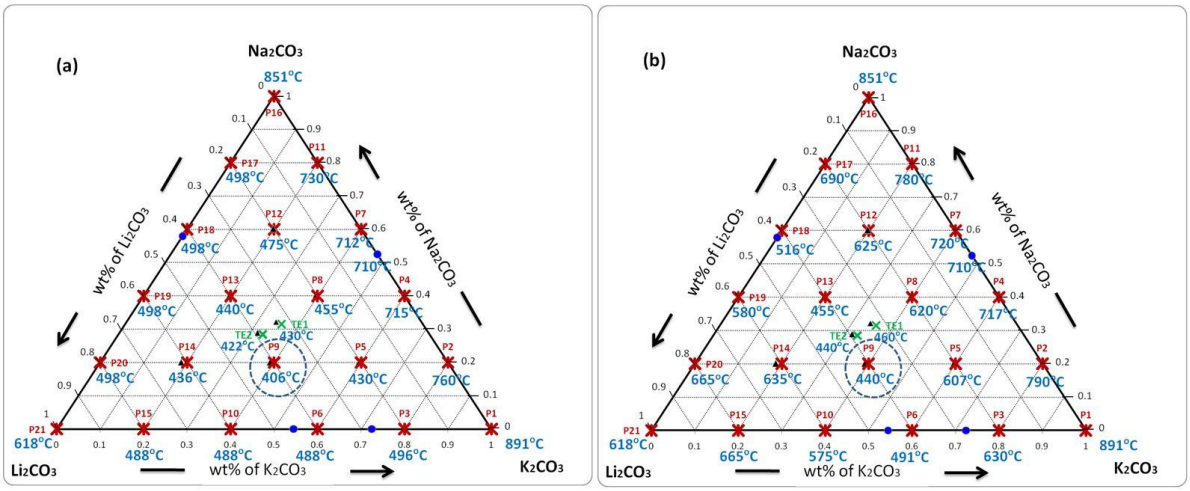


Fig. 2. (a) Solidus Temperatures (b) Liquidus Temperatures, of mixed alkali-metal carbonate salts at different wt.% compositions of Li_2CO_3, Na_2CO_3 and K_2CO_3

2.3. Selection of a Catalyst and Preparation

Some noble metal such as Rh, Ru, and Ir are very active for methane reforming. However, in commercial and industrial scale, it is not preferable as such expensive catalysts, especially, for methane dry reforming, would be technically and economically very difficult to reuse and recycle, in comparison with a conventional fixed bed reactor. The commonly cost effective catalysts used are Ni, Fe, Cu or W metal catalysts. (T. Kodama. 2001)[8]. Kodama has examined Ni, Fe, Cu or W metals, supported on Al_2O_3 for activity and selectivity at 1223K. The most active and selective catalyst was the $Ni - Al_2O_3$ catalyst for methane dry reforming in a molten carbonate salt bath for use in STC Processes.

In this study, three types of Ni-Loading (10%, 15% & 20% wt.%) supported by $\alpha - Al_2O_3$ catalysts, were analyzed. The coke amount on the catalyst was examined by means of the mole balanced equations as would be explained in next section. The supported nickel catalyst on $\alpha - Al_2O_3$ was prepared by impregnation using Nickel (II) nitrate solution.

2.3.1 Catalyst Characterization - Ni Particle size and X-ray diffraction

In order to determine the surface area of the used catalysts, the X-ray diffraction spectra were obtained with HZG-4S apparatus ,Cu-K α radiation (λ =1.5418 $^{\circ}$ A)) with graphite monochromator put on diffraction beam. The scanning diffraction pictures were carried out in the 2θ range of $20^o - 80^o$ with 0.2^o step per 3s time of accumulation in a point.

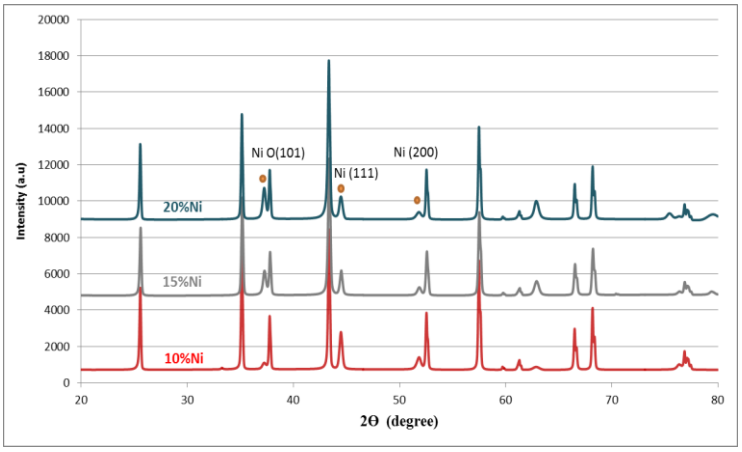


Fig. 3. XRD Patterns of Ni% (10%, 15% & 20 wt. %) Loading Catalysts supported on Al_2O_3

After the calcination treatment, dispersed Ni particles are presented in the oxide forms, Fig.3. The Ni% loading and calcination treatment does

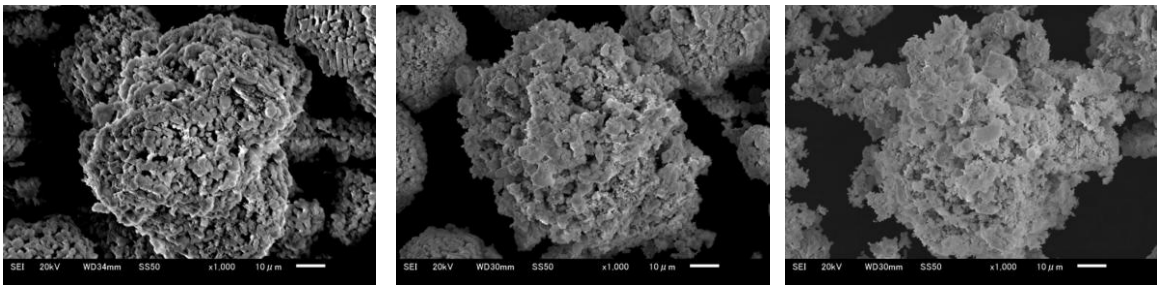
not significantly change the phase structure of the support. However, The Ni and NiO crystallite size can be estimated from the Full Width at Half Maximum (FWHM) of the their corresponding peaks using Scherrer equation. The results is given in Table 1.

	20 % Ni - Al_2O_3			15 % Ni - Al_2O_3			10 % Ni - Al_2O_3		
	2Θ (deg.)	FWHM (deg.)	Crystallite size (nm)	2Θ (deg.)	FWHM (deg.)	Crystallite size (nm)	2Θ (deg.)	FWHM (deg.)	Crystallite size (nm)
Ni (111)	44.506	0.243	36.922	44.419	0.319	28.117	44.457	0.278	32.268
Ni (200)	51.836	0.362	25.504	51.790	0.506	18.242	51.813	0.419	22.032
NiO (101)	37.240	0.291	30.112	37.223	0.310	28.265	37.201	0.380	23.057

Table 1. Crystallite sizes estimation of Ni% (10%, 15% & 20wt%) loading catalysts on Al_2O_3

2.3.2 Catalyst Characterization - Transmission Electronic Microscopy (TEM)

The TEM images of fresh Ni% loading of (10%, 15% & 20 – Al_2O_3 wt.%) catalysts were taken with JSM-6510LA – Analytical Scanning Electron Microscope, as shown in Fig.4, with magnification of $\times 1000$, to investigate the surface morphology and crystallinity of the fresh catalysts.



(a) (b) (c)

Fig. 4. TEM images of the Nickel metal loading catalysts before the reactions (a) 10% Ni-Al_2O_3 (b) 15% Ni-Al_2O_3 (c) 20% Ni-Al_2O_3

2.4. Theory of Methane Conversion

Given the following real-world reaction scheme for the methane dry reforming;

$$CH_4 + CO_2 \rightarrow \alpha CH_4 + \beta CO_2 + \gamma CO + \delta H_2 + \varepsilon C_2H_2 + \epsilon C_2H_4 + \theta C_2H_6 + \vartheta H_2O + \mu O_2 + \pi C \quad (2)$$

Where α, β ... π are the stoichiometric coefficients

For methane reforming reaction with CO_2, there are 10 species (CH_4, CO_2, CO, H_2, C_2H_2, C_2H_4, C2H6, H2O, O2, C and 3 elements (C, H, and O). If Ac denotes the total concentrations of the outlet flow of all species containing carbon element except Carbon black itself, B_o denotes species containing oxygen element except H_2O and C_H denotes species containing Hydrogen element except H_2O, as follows;

$$A_c = [CH_4] + [CO_2] + [CO] + 2[C_2H_2] + 2[C_2H_4] + 2[C_2H_6] \quad (3)$$

$$B_o = [CO] + 2[CO_2] + 2[O] \quad (4)$$

$$C_H = 2[H_2] + 4[CH_4] + 2[C_2H_2] + 4[C_2H_4] + 6[C_2H_6] \quad (5)$$

The quantities of the two unknown species of carbon black deposition and the H_2O formation can be determined using the mole balanced equation on C, H, and O as follows;

$$\frac{C}{O} = \frac{A_c+[C]}{B_o+[H_2O]} = a \quad (6)$$

$$\frac{C}{H} = \frac{A_c+[C]}{C_H+2[H_2O]} = b \quad (7)$$

The chemical conversion of CH_4, is defined as the mole ratio of CH_4 decomposed to CH_4 in the feed. However, the CH_4 conversion can be defined with respect to the outlet concentrations of species as follows;

$$Conversion\ (CH_4)\% = 1 - \frac{[CH_4]}{(A_c+[C])\times n} \quad (8)$$

The CO_2 conversion can be defined in same manner as follow;

$$\text{Conversion } (CO_2)\% = 1 - \frac{[CO_2]}{(A_c+[C])\times m} \quad (9)$$

Where the values of *n* and *m* are related to intial conditions of $CH_4:CO_2$, in such that *n* defines the theoretical methane concentration in terms of a fraction of intial concentations of carbon contained species. Similarly, *m* defines the theoretical CO_2 concentration in terms of a fraction of intial concentations of carbon contained species. These values of *a*, *b*, *n* and *m* are shown in Table 2

	a	***b***	***n***	***m***
CH_4:CO_2 Ratio = 1:1	1	1/2	1/2	1/2
CH_4:CO_2 Ratio = 1:2	3/4	3/4	1/3	2/3
CH_4:CO_2 Ratio = 1:3	2/3	1	1/4	3/4

Table 2. Values of *a, b, n* and *m* for different CH_4:CO_2 Ratio

The H_2 yield, is defined as the mole ratio of H_2 in the gas products measured by DGMS to the theoretically maximum H_2 when the reaction reaches completion:

$$\text{Yield } (H_2)\% = \frac{(H_2)_{out}}{2\times (CH_4)_{in}} \times 100 \quad (10)$$

The CO yield is defined as;

$$\text{Yield } (CO)\% = \frac{(CO)_{out}}{(CH_4)_{in}+(CO_2)_{in}} \times 100 \quad (11)$$

The H_2O yield is defined as;

$$Yield\ (H_2O)\% = \frac{(H_2O)_{out}}{2\times (CH_4)_{in}} \times 100 \quad (12)$$

3. Results and Discussions

3.1. Influence of Nickel Loading Catalysts

The influence of Ni loading on the conversions of methane and H_2 yield at reaction temperature of 800^oC, and the flow of both CH_4 and CO_2 of ratio of 1:1 at 50 mL/min, is shown in Fig.5, in which data was obtained after 4 hours reaction. As expected, the conversion is related to the metal loading. The methane conversion increased from 45% to 69% as the Ni % loading decreased from 20% to 10%. However, the H_2 yield exhibited the highest at Ni% loading of 15%. The catalytic activity revealed increasing during the first 4 hrs reaction and found active for CH_4 dry reforming.

Fig.6 shows the effect of reaction temperature from $600-800^oC$ on the methane conversions and H_2 yield. They were significently increased as the reaction temperature increased. The methane conversion of 15% Ni loading was nearly same as 20% Ni loading in low reaction temperatures. However, in high temperatures, the catalytic activity increased toward the highest methane conversion and hydrogen yield.

The influence of Ni% loading on the carbon deposition is illustrated in Fig.7. 15%Ni-Al_2O_3 catalyst showed the lowest carbon deposition in grams per mole of methane. The effect of reaction temperature on coke formation is significient at relatively high temperatures as the methane conversions (or methane cracking reactions) are the highest .

3.2. Effect of Excess CO_2 on Methane Dry Reforming

The feed flow ratio of CO_2/CH_4 was changed to 3:1, 2:1 & 1:1, at constant reaction temperature of 800^oC with constant CH_4 flow rate of 20 ml/min and constant total inlet flow rate of 100 ml/min by varying the inert Ar gas, that to avoid the effect of flow rates and residence time on methane conversion. The catalyst used is 15% Ni - Al_2O_3 catalyst

Fig.8 illustrates the influence of excess CO_2 on methane dry reforming reaction. As the $CO_2:CH_4$ ratio increased from 1:1 to 3:1, the conversion of methane increases from 73% to 89%, whereas the H_2 yield decreased from 46% to 22%. Along with the increase of methane conversion, both of H_2O% and CO% yields are also increasing, as shown in Fig.9.

It clearly understandable from the positive value of heat of formation of Reverse Water Gas Shift (RWGS) reaction, equation 13, which is much lower than methane dry reforming reaction, equation 1. This indicates that the side reaction of RWGS reaction takes place faster than the main reaction. In same context, it is much easier for CO_2 to react with H_2 than the deposited C, equation 14

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^{o}_{@\,298K} = +41\ KJ/mol \qquad (13)$$

$$CO_2 + C \rightarrow 2CO \qquad \Delta H^{o}_{@\,298K} = +172\ KJ/mol \qquad (14)$$

As a result, the H_2 (desire product) formed from the methane dry reforming process will react immediately with CO_2 to produce H_2O (undesired product) and directly reduces the overall H_2 yield and increases CO yield. This is in full agreement with experimental laboratory results in which have showed that CO_2 conversion was higher than that of CH_4; higher CO yield compared to H_2 yield; and CO: H_2 ratio was increasing as $CO_2:CH_4$ ratio increased. Therefore, the understanding of the effect of water formation from side reactions is important as to determine the optimum conditions in order to avoid any reductions in product selectivities, yields as well as the syngas product ratio.

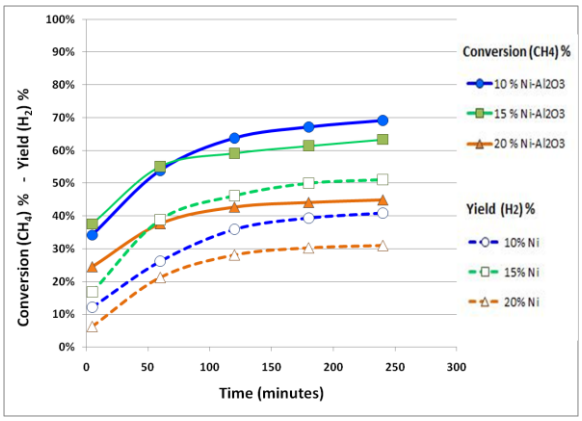


Fig.5. Effect of Ni% loading on methane dry reforming with CO_2 at reaction temperature of 800°C, and CH_4 and CO_2 flow of ratio of 1:1 at 50 mL/min, during 4 hrs reaction time.

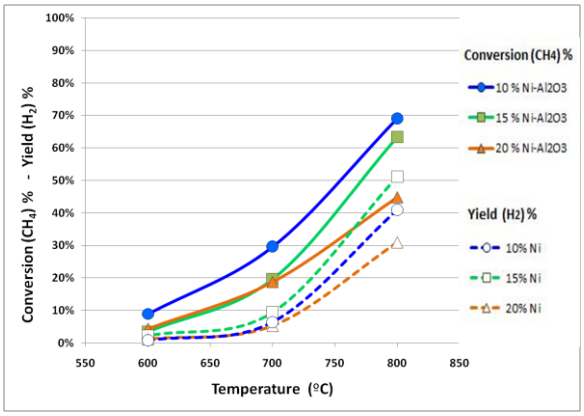


Fig.6. Effect of reaction temperatures, different Ni% loading on methane dry reforming with CO_2 at CH_4 and CO_2 flow of ratio of 1:1 at 50 mL/min

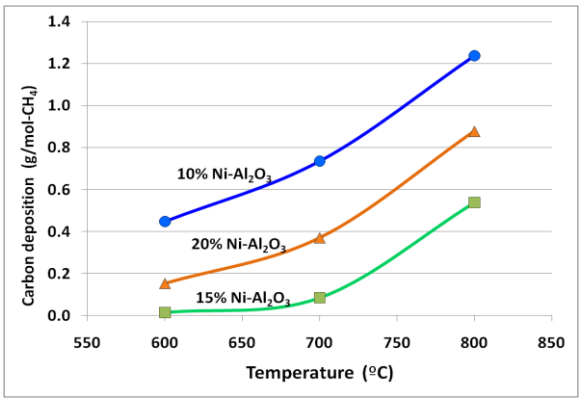


Fig.7. Carbon deposition in g/mole-methane, for different Ni% loading at various temperatures with flow rates of both CH_4 and CO_2 of ratio of 1:1 at 50 mL/min

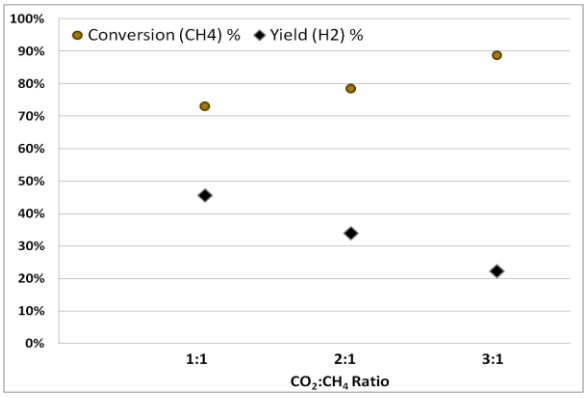


Fig.8. Carbon deposition in g/mole-methane, for different Ni% loading at various temperatures with flow rates of both CH_4 and CO_2 of ratio of 1:1 at 50 mL/min

Fig.10 shows the effect of excess CO_2 on carbon deposition. As the $CO_2:CH_4$ ratio increased from 1:1 to 3:1, the carbon deposition, in grams per mole of methane, is decreased. The excess CO_2 provides higher reaction rates of Boudouard reaction or carbon oxidation reaction, in accordance to equation 14, with an increasing in CO% yield, as in full agreement with the experimental results.

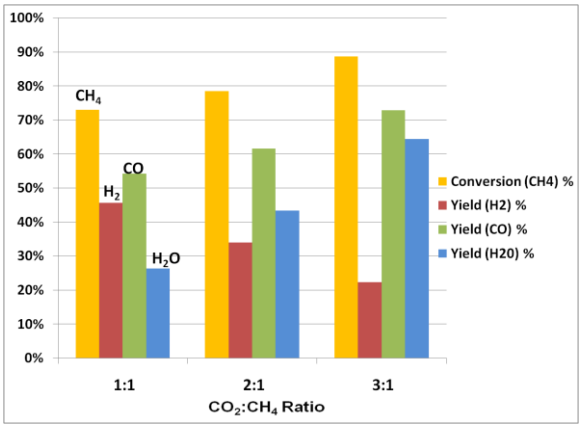


Fig.9. Conversion (CH_4)%, Yield (H_2)%, Yield (CO)%, and Yield (H_2O)% for various CO_2/CH_4 ratios, at constant reaction temperature of 800^oC with constant CH_4 flow rate of 20 ml/min and constant total inlet flow rate of 100 ml/min

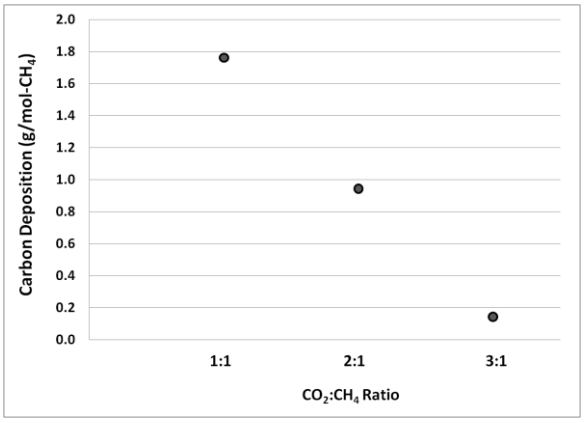


Fig.10. Carbon deposition in g/mole-methane for various CO_2/CH_4ratios, at constant reaction temperature of 800^oC with constant CH_4 flow rate of 20 ml/min and constant total inlet flow rate of 100 ml/min

3.3. Effect of Flow Rates on Methane Dry Reforming

In accordance to the results of previous section, the flow rates of the selected CO_2/CH_4 of ratio 2:1 was changed to (CH_4 flow rate of 15, 30 & 50mL/min) at constant reaction temperature of 800^oC. The Ar flow rate was kept constant at 30ml/min, and the catalyst used was 15% Ni - Al_2O_3. The methane conversion and hydrogen yield are decreasing as the total flow rate increases, as shown in Fig.11. The methane conversion decreased from 87% to 57% whereas hydrogen yield decreased from 40 to 9%.

Water formation is likely independent on the effect of total flow rates of the CO_2/CH_4 of ratio 2:1, as shown in Fig. 12. However, as the flow rate is decreasing, the CO% yield is significantly increased from 28% to 79%, revealing the positive effect of low flow rates on increasing the methane conversions, hydrogen and carbon monoxide yields. This maybe attributed to higher residence times. Consequently, this effect gives the opportunity for higher reaction rates of Boudouard reaction , shown in equation 14, for lower carbon deposition per mole methane. The result is illustrated in Fig.13

Fig.12, also shows the amount of stored energy in forms of H_2 and CO in $KJ/mol-CH_4$ that can be estimated using the differences in the amount of heat released from the combusted methane of (-802 $KJ/mol-CH_4$) and the amount of heat that can be released from the produced H_2 & CO during methane conversions. It can be noted that in case of higher flow rates of 50 and 30 ml/min, there is no energy storage as most of methane is converted to H_2O, whereas at methane flow rate of 15ml/min the thermal storage energy in forms of H_2 and CO of approximately $156 KJ/mol_{CH_4}$with a storage efficiency of 63.1%.

3.4. Effect of Catalyst/ Molten Salt Ratio on Methane Dry Reforming

Fig.14 shows the methane conversion and $H_2:CO$ production ratio, at constant reaction temperature of 800^oC and constant flow rates of both CH_4 and CO_2 of ratio of 1:1 at 50 mL/min, the amount of catalyst (10% Ni-Al2O_3) was changed with respect to molten salts (Cat./MS = 0.25, 0.5, 0.75, 1.0 & 1.25). The methane conversion was found increasing as the Cat./molten salts ratio is increased. It can be noted that the stoichiometric $H_2:CO$ production ratio of unity can be achieved at Cat./MS ratio between 1-1.25.

The curves of Fig.14 has shown nearly the same trends of reported results of T. Kodama, T. Koyanagi, 2001, of their experimental data of reformed methane with CO_2 in (25g) alkali-carbonates Na_2CO_3, K_2CO_3 (weight ratio = 1:1) at 1223K for a flow rate of the $CH_4/$ CO_2 feed was 200 ml/min.

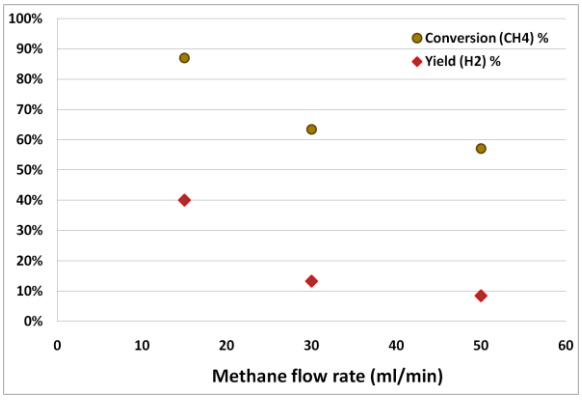


Fig.11. Effect of total flow rate (methane flow rate) of CO_2/CH_4 ratio of 2:1, at constant reaction temperature of 800^oC with constant Ar flow rate of 30 ml/min

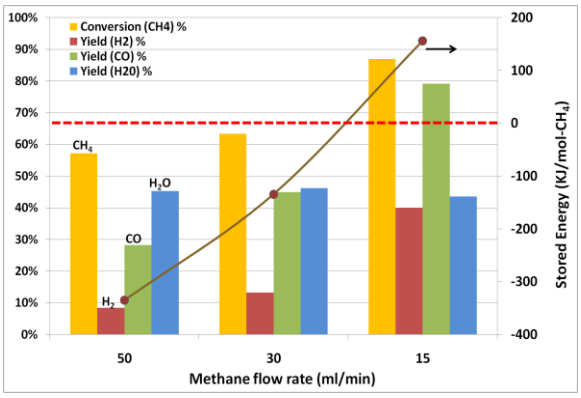


Fig.12. Conversion $(CH_4)\%$, Yield $(H_2)\%$, Yield $(CO)\%$, and Yield $(H_2O)\%$ and the amount of stored Energy (KJ/mol_{CH_4}) with the effect of total flow rate (methane flow rate) of CO_2/CH_4 ratio of 2:1, at const. reaction temperature of 800^oC with constant Ar flow rate of 30 ml/min - 15% Ni-Al_2O_3 catalyst

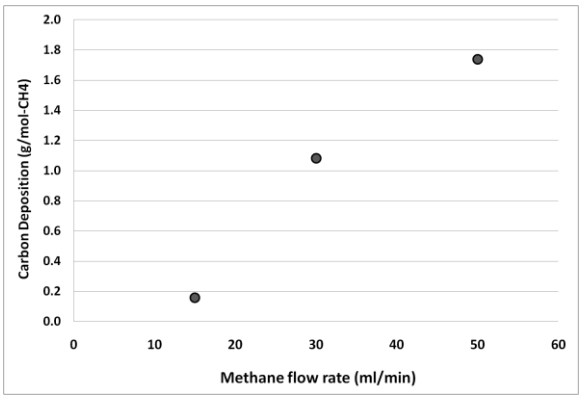


Fig.13. Carbon deposition in g/mole-methane with the effect of total flow rate (methane flow rate) of CO_2/CH_4 ratio of 2:1, at constant reaction temperature of 800^oC with constant Ar flow rate of 30ml/min - 15% Ni - Al_2O_3 catalyst

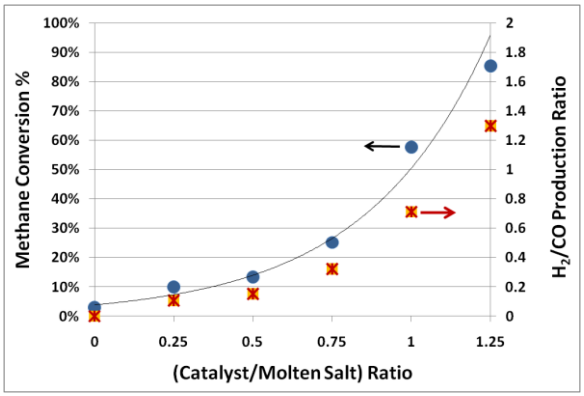


Fig.14. CH_4 conversion and $H_2:CO$ production ratio as a function of (Cat./MS) ratio with a fixed amount of Na_2CO_3, K_2CO_3 and Li_2CO_3 (1:2:2), using 10% Ni - Al_2O_3 catalyst at reaction temperature of 800^oC, and the flow of both CH_4 and CO_2 of ratio of 1:1 at 50 mL/min, during 2 hrs reaction time.

4. Conclusion

Conceptual idea of DCBR was proposed to promote solar thermal energy storage, integrated with methane dry reforming, with a higher energy conversional capacity, higher thermal efficiency and greater simplicity of construction. The experimental results show the increase of CO_2/CH_4 ratio in terms of higher methane conversion and CO yield, whereas the $H_2:CO$ production ratio was significantly decreasing, attributed to increase in water formation due to RWGS reaction. While, the carbon deposition is decreasing as per the theoretical results. The estimation of thermal energy stored chemically revealed a capacity of the storage efficiency of 63.1% at low temperatures of $600-800^oC$. However, this figure shall be increased at higher reaction temperatures and lower flow rates, as the RWGS reaction would be decreased.

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