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Solar Methane Reforming Microreactor Proof-Of-Concept With A 2X2 Array On A Full-Scale Dish

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Abstract. Researchers from Université de Sherbrooke have developed a new generation of high efficiency Solar Microreactor to harvest the power of the sun for hydrogen production. This paper presents the architecture, the manufacturing and assembly of this highly integrated system that incorporates in a monolithic block the heat exchangers, catalytic bed and manifolds. Miniaturization of the system provides high heat and mass transfer capabilities and can easily be assembled into a matrix to cover the focal point of any Solar Concentrator. Performances of the Microreactor is first investigated in a laboratory using a high flux solar simulator to plot an efficiency map for a dry methane reforming test under different combinations of reagent mass flow and reaction temperatures. This map is then used as a benchmark for outside tests in order to evaluate the real-condition efficiency of such microreactor matrix. Outside tests were performed with the Université de Sherbrooke's 100 kW SpaceWatt solar concentrator. It is estimated that the efficiency reaches up to 54 % for the matrix of reactor in real condition operation for an estimated heat flux of 520 kW/m^2 compared to the measured value of 71% in laboratory conditions for a single reactor with a heat flux of 800 kW/m^2.

Keywords: Dry Methane Reforming, Microreactor Array, Solar Concentrator, High Flux Solar Simulator

1. Introduction

Hydrogen production by methane reforming is responsible for 3% of worldwide CO2 emissions with natural gas being the primary energy source required by the endothermic reaction [1]. Replacing the combustion of methane by renewable energy has the potential to reduce 1% of the global CO2 emission [2], with solar energy being one of the most attractive power sources.

Despite its inherent thermodynamic benefits [3], there are no commercial solar-based SMR plants for hydrogen production. Previous attempts at implementing this production pathway have relied either on minimally integrated processes [4], or custom solar concentrations (e.g., dish system [5]), leading to high capital expenditures.

In order to drive down the costs associated with solar aided methane reforming, researchers from Université de Sherbrooke have developed a new generation of high efficiency solar microreactor [6]. The highly integrated system incorporates in a monolithic

block a heat exchanger, a catalytic bed, manifolds and vaporizers allowing both Dry Methane Reforming (DMR) and Steam Methane Reforming (SMR) capabilities. Miniaturization of the system enables high heat and mass transfer capabilities, allowing the system to absorb a high heat flux (>900 kW/m^2) at high efficiency (>60%). With its high efficiency and power density, these highly scalable reactors have a very small footprint and thus can be assembled into a matrix to cover the focal point of any solar concentrator, allowing progressive scale-up of the system and eventually be installed on a solar power tower.

This paper presents the experimental demonstration in real-condition operation of microreactors assembled in a 2x2 array. The first section highlights the anatomy of the microreactor and its manufacturing process. Pre-qualifying test and characterization of each reactor are then described for laboratory conditions before assembly into a matrix. Experimental results are finally presented and discussed for its full-scale dish integration.

2. Microreactor Architecture, Manufacturing, and Assembly

The array is composed of four (2x2) identical microreactors developed at Université de Sherbrooke and shown in Figure 1. The head of the reactor has two input ports for reagents (CH4, CO2, H2O) whether it is for dry methane reforming (DMR) or steam methane reforming (SMR), and one exit port for the syngas. Despite this dual reaction capability, only DMR is demonstrated in this article. A heat exchanger preheats the reagents and increases the efficiency. The catalytic zone is where the chemical reaction occurs. It is composed of micro channels in which a catalyst (Ni/Al2O3 spinel-based 40µm powder) is inserted before sealing with TIG welding. The energy needed by the reaction is supplied by concentrated solar heat flux at the bottom surface of the reactor and conducted through the internal fins. The reagent plenum allows to uniformly distribute gases into the catalyst chambers being heated by the side fins.

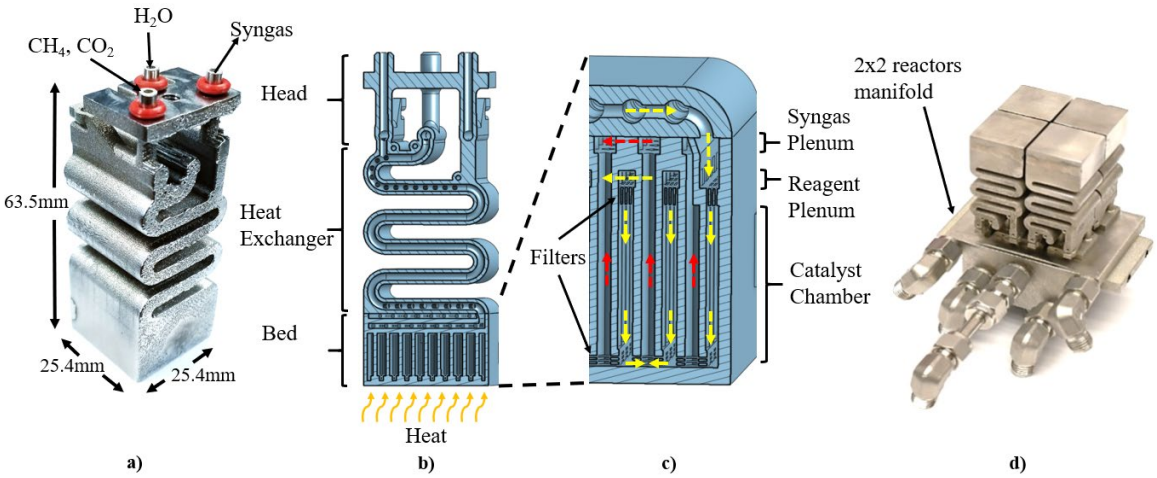

Figure 1. a) 3D printed Inconel 718 solar reactor, b) side cut of the reactor, c) catalytic bed architecture, and d) final assembly of the 2x2 microreactor array before instrumentation and field test.

Reactors are built with a 3D printer (MLab 200R) that uses a Direct Metal Laser Melting (DMLM) process. This method allows to manufacture small and complex geometries, and is well suited for fast iteration in the design process. Reactors are made of Inconel 718 since high temperature resistance is required.

After manufacturing and annealing, each reactor is prequalified starting with a pressure test to ensure no leak is present after welding. Then, head loss measurements are individually performed on each reactor to make sure that the parallel flows into the 2x2 manifold is also

equal. Reactors are then activated (Figure 2) using a 2.5-kW High Flux Solar Simulator (HFSS) based on the approach proposed by Bucknell University [7].

The activation is carried by flowing 1000 Standard cubic centimeters per minute (SCCM) CH4 and 1100 SCCM CO2 for one hour, with a temperature of 1200°C at the surface of the reactor. Reactors are finally assembled on a common 3D-printed SS-316 manifold to create a 5 cm x 5 cm area, composed of four reactors, amounting to a thermal power of 2.5 kW (Figure 1 d). This prototype, called RGP 2.5 (2.5 kW Reactor Grid Plate), is then instrumented and installed on a solar receiver.

3. Microreactor Characterization

The HFSS is used to activate the catalyst and map the efficiency of the reactor. The setup (Figure 2) is made of a 2.5 kW metal halide lamp and two optical concentrators. The reactor is connected to a manifold and instrumented with thermocouples before being installed at the focus. Mass flow controllers from Alicat are used to precisely adjust each input flow, whereas the syngas is analyzed using Fourier-transform infrared spectroscopy (FTIR) Tensor 27 from Bruker.

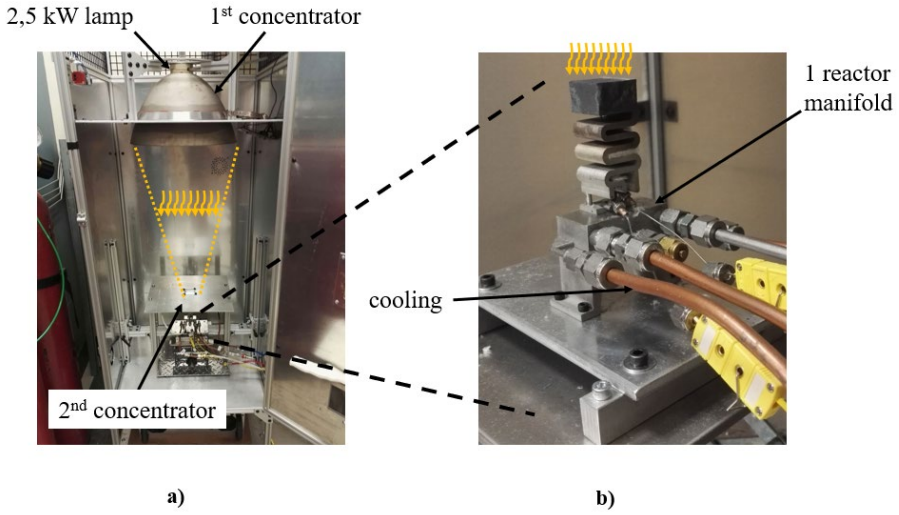

Figure 2. a) Reactor into the HFSS and b) close view on the reactor maintained by its manifold.

In order to characterize the power output from the HFFS, a water calorimetry test was performed on a 1 square inch surface to map the heat flux at the focus. A maximum concentration of 840X (1X = 1 kW/m^2) was achieved at 100% power. The efficiency of the reactor was characterized at several reagent mass-flow rates and steady-state temperatures for the DMR reaction. During experiments, CH4 is injected with flows ranging from 0.5 to 2 standard liter per minute (SLPM), and the required CO2 flow is adjusted in order to get a CO2:CH4 ratio of 1.1. For each flow, lamp power is modified until stable temperatures of 1070°C, 1110°C, 1150°C and 1200°C are reached at 1 mm under the radiated surface. The pressure at the input ports of the microreactor varied between 1.4 and 4 bar as a function of the mass flow and the temperature of the DMR reaction.

The process efficiency is defined as the variation of enthalpy of formation between the products and the reagents at 25°C divided by total energy provided to the process:

$$\eta_{process} = \frac{\Delta h_{25}}{q_{in}} \quad (1)$$

where h is the specific enthalpy and q_{in} the incoming power sent to the reactor. Using a mass balance on carbon, the methane conversion X_{CH_4} is defined by:

$$X_{CH_4} = 1 - \frac{CH_4}{CH_4 + CO_2 + CO} \quad (2)$$

For each combination of flow and temperature tested, the syngas analysis gave a 100% methane conversion. The resulting efficiency map (Figure 3) is the benchmark used to evaluate tests on the full-scale dish.

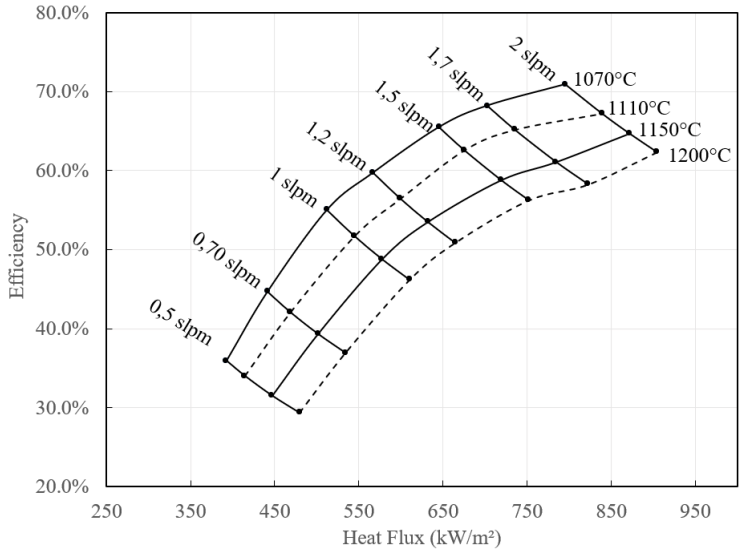

Figure 3. Efficiency map of one microreactor under HFSS for DMR reaction at different heat flux and CH4 flows (0.5 to 2 SLPM) with CO2:CH4 ratio of 1.1:1.

This map shows that the efficiency reaches as high as 71%. It also reveals that the efficiency is mostly driven by the heat flux. This tendency illustrates that, for a given temperature, heat lost to the environment remains essentially constant while the incoming power and the energy absorbed by the DMR reaction increase, raising the value of efficiency. Finally, the large efficiency gain encountered while operating at lower temperature for a given heat flux highlights the interest of reducing the temperature of operation as much as possible if no conversion limitations occur.

4. Outdoor Experimental Setup

For real-condition operation, the RGP 2.5 is installed on the Université de Sherbrooke's 100 kW SpaceWatt solar concentrator (Figure 4 a). The RGP 2.5 is placed at one of the two concentrator's targets (50 kW each). Data acquisition (NI Compact RIO), security valves and sensors are at the top of the concentrator (Figure 4 b). The system control panel, gas and water supply, as well as gas sampling and analysis devices are located at the bottom of the system for easy access during operation (Figure 4 c).

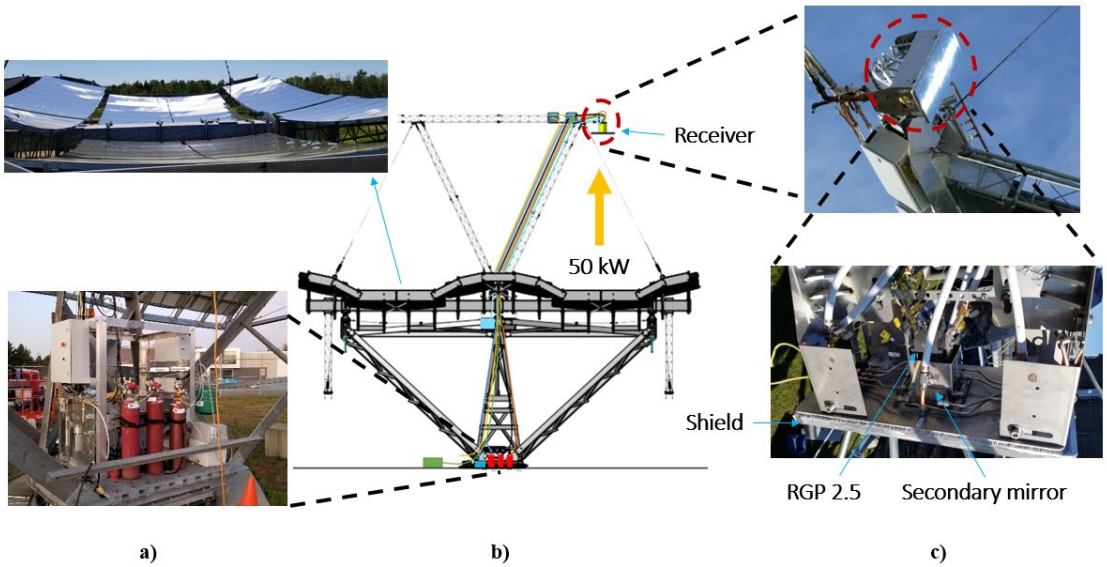

Figure 4. Université de Sherbrooke's 100 kW SpaceWatt solar concentrator: a) system's control panel supplies and gas sampling/analysis, b) global schematic, and c) RGP 2.5 installed on the concentrator with its auxiliary systems.

For both in-lab and outside tests, hydraulic set-up is similar besides the heat source (sun versus lamp) and the cooling management. Figure 5 shows the simplified hydraulic circuit of the solar dish setup. Since the RGP2.5 is designed for 2.5 kW of endothermic chemical reaction, the excess energy coming from the sun is first managed by covering some mirrors of the solar dish (first concentrator). Then a reflective liquid-cooled shield is used to protect parts of the receiver that are not meant to sustain the high temperature (electronics, structure, piping…) from concentrated solar radiation. At lower concentrations, from 375 X to 625 X, the shield is able to reflect 98% of the radiation with a liquid cooling loop that maintains its surface temperature below 100° C. To get high solar concentrations on the reactors, a secondary mirror is installed between the array and the shield with a gain of 3.4. The idea behind the secondary concentrator is to reach high solar concentrations on the reactor while facilitating the management of excess heat at lower concentration around the reactors. The secondary mirrors and the reactors' manifold are also liquid cooled with parallel circuits.

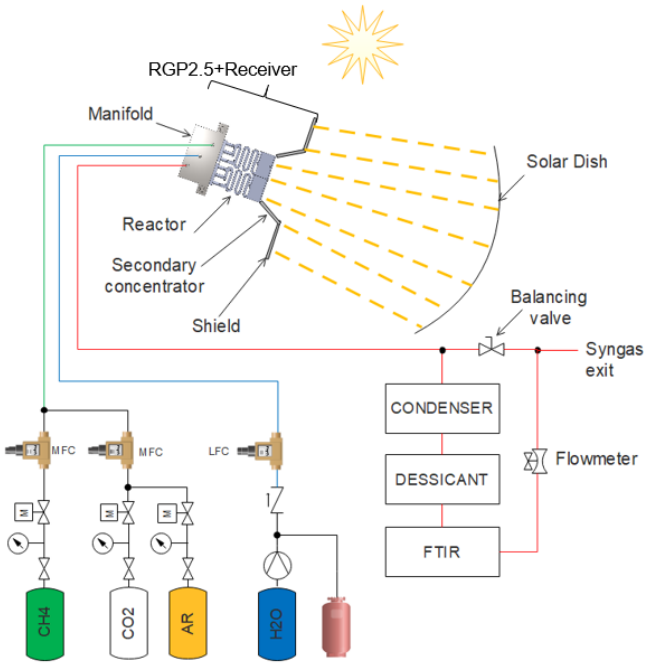

Figure 5. Simplified hydraulic schematic of the 2x2 microreactor array installed on the Solar Dish (cooling not shown).

The DMR reaction is made at low pressure (under 4 bar) only to overcome the pressure loss in the reactors and piping. Pressurized gas tanks are used, combined with precise mass flow controllers (MFC) to bring the methane and carbon dioxide needed for DMR. Argon is only used in the warm-up and cool down sequences. Motorized valves allowed to choose what gases to mix. SMR reaction could also be done with this installation but is not covered in this paper. All the reagents are brought to the four reactors by a common manifold which meant that the flow distribution between them would be equal only if they have the same pressure drop. After exiting the reactor, part of the gas is redirected to a condenser and a desiccant for analysis with the FTIR while the remaining gas is vented outside.

5. Outdoor Test Results

The matrix has been tested under a partially cloudy day of fall 2019 in Sherbrooke, Canada. Two full tests were achieved that day, one in the morning, and the second in the afternoon. First, the reactors were heated up under argon flow by moving the solar receiver in and out of focus. This allows to slowly heat the reactor and prevent overheating. However, this method has the disadvantage to create a non-uniform radiant flux, thus an unequal temperature profile over the array as it can be seen on Figure 6 a). Following the heat-up, the array is put fully on focus. Since the heat flux on the reactors cannot be regulated, the only way to control the reactors' temperature is by adjusting the reagent flow, which took about 2 minutes to achieve and caused the first drop of temperature after 35 minutes in Figure 6 a). Temperature uniformity is much better between reactors when the array is maintained on focus.

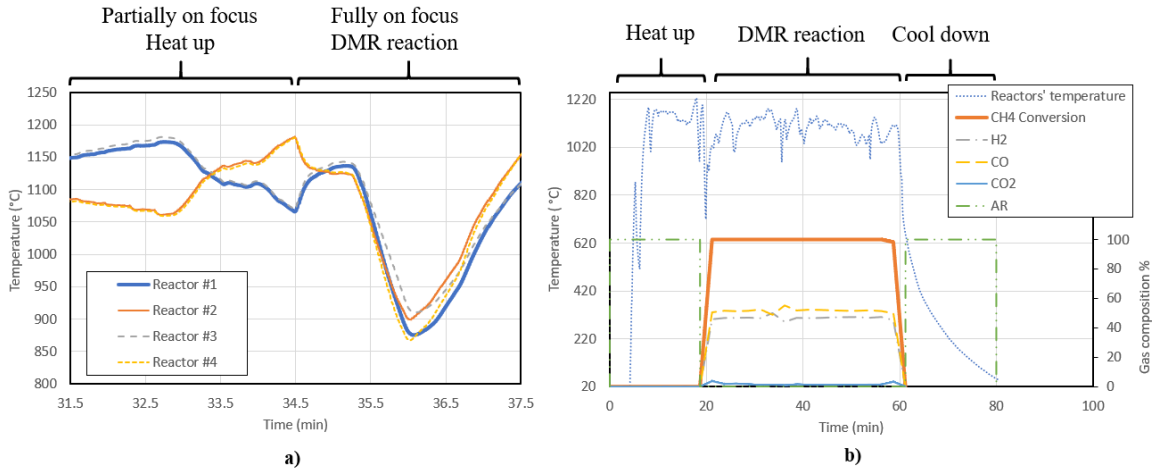

Figure 6. a) Temperature uniformity over the array of reactors for heat up and DMR sequences, and b) temperature profile over a complete test sequence and gas composition measured at the exit of the RGP2.5.

Figure 6 b) shows the mean temperature between reactors for a full test, the syngas composition and the CH4 conversion. DMR is done with a CO2:CH4 ratio of 1.1. The array reaches a quasi-steady state between 1050°C and 1200°C after a short 4-minute ramp-up time (heat up), whereas the cool down (out of focus) takes about 20 min under argon flow. During the test, variations of temperature were essentially caused by clouds turning down the DNI (Direct Normal Incidence) and thus the heat flux to near zero. These fluctuations were hard to manage at that time since reagent flow were manually adjusted by the operator. Nevertheless, it was possible to maintain high temperature and reach 100% of CH4 conversion. The ratio H2:CO is near the theoretical value of 1 in DMR reaction, which implies that other side reactions are negligible.

Since it is hard to exactly quantify the amount of energy transmitted by the solar dish to the RGP 2.5, one way is to use the benchmark efficiency map (Figure 3). Thus, for a given flow of CH4 and a measured temperature at the reactor, it is possible to estimate both efficiency and heat flux for short steady temperature. During the test, total CH4 input flow is ranging from 2 to 8 SLPM, and it is assumed that the reagent flow is equally split between reactors (0.5 SLPM to 2 SLPM per reactor). The maximum heat flux estimated is 560 kW/m^2 which is less than what was expected even with high DNI obtained during the test (up to 700 W/m^2 measured with a RaZON Solar Monitoring system), but this could be influenced by many variables such as mirrors cleanliness, real first and secondary mirrors' concentration, real DNI, good focus, heat flux uniformity, etc. The maximum efficiency reaches up to 54% with a heat flux of 520 kW/m^2, which is promising for first tests even if it is lower than the maximum that the reactor can achieve. However, this can be explained by not being able to feed a high flow of CH4 during enough time to consider a steady temperature.

6. Summary and Conclusions

These results highlight the potential to operate a matrix of microreactors in a full-scale solar dish to produce hydrogen with a high efficiency. The reagents flow was roughly controlled without compromising the CH4 conversion for temperatures above 1000°C. It was shown that the four reactors could operate at similar temperatures when proper solar tracking is achieved. The RGP 2.5 performed with efficiency up to 54% in DMR, but could be higher if steady temperatures are achieved. Demonstration was made for a small 2x2 array of microreactors, but could be scaled up to cover a larger focal spot such as in a solar tower. It is expected that the heat flux should be uniform over the array, otherwise a zoning control may need to be considered. Having a better control of reagent flow under fluctuating DNI would help reducing reactors' temperature variations and thus allows to work in a lower range of temperatures.

Consequently, this would lead to a better efficiency and maximizing the power density. Further developments are in progress to define operation limits of the reactor in DMR as well as in SMR. A 100% electrical alternative using microreactor array is also being evaluated to compare advantages and inconvenient of both methods.

Data Availability Statement

Data supporting the results from this article can be assessed by making a request to the author. The availability of data is not restricted.

Author contributions

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Jean-François Dufault : Conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, visualization

Jean-François Peloquin : Data curation, formal analysis, investigation, methodology, visualization

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Ignacio Jorge Castellanos-Beltran : Data curation, formal analysis, investigation, methodology, software

Nadi Braidy : Methodology, resources, supervision

Luc G. Fréchette : Conceptualization, funding acquisition, methodology, resources, supervision

Mathieu Picard : Conceptualization, funding acquisition, methodology, resources, supervision

Competing interests

The authors declare that they have no competing interests.

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