Testing of a 3D-Printed Solar Micro-Reactor for Hydrogen Production via Natural Gas Reforming

Paul Camus, J-F. Dufault, D. Mehanovic, N. Braidy, L. G. Fréchette and M. Picard
Institut Interdisciplinaire d’Innovation Technologique (3IT), Université de Sherbrooke, 3000 Boulevard de l’Université, Sherbrooke, J1K 0A5, Québec, Canada
Paul.Camus@Usherbrooke.ca

Abstract. This paper presents the design, fabrication, and successful real-condition testing of a solar micro-reactor for hydrogen synthesis via steam methane reforming (SMR). This micro-reactor integrates all the sub-processes necessary for SMR in a network of small three-dimensional channels, making it well-suited for implementation on the commercially available parabolic trough solar concentrators. Additive manufacturing was used to create an operational prototype of this micro-reactor. The prototype was integrated to a parabolic mirror for solar concentration, and tested in real conditions. Complete methane conversion to syngas was obtained with an absorbed solar radiation equivalent to 240 suns, which demonstrates the feasibility of solar SMR at moderate solar concentration.

1. Introduction
Renewable hydrogen has the potential to become an excellent energy carrier and replace fossil fuels. It is also already relevant in industrial applications to reduce their CO₂ emissions. However, the vast majority of hydrogen synthesized worldwide comes from conventional steam methane reforming (SMR), which is an endothermic reaction involving the combustion of approximately 30% of the methane feedstock available for hydrogen production. This global endothermic process of SMR is summarized by:

\[ CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H = 165 \text{ kJ/mol} \] (1)

This reaction is greatly accelerated by using a catalyst, but it remains necessary to provide heat, which is conventionally performed through natural gas combustion, a process contributing significantly to CO₂ emissions. To avoid these emissions, a renewable source of energy can be used as a heat source. Precisely, solar energy can be concentrated to reach a power density high enough to sustain the endothermic SMR reaction. Although solar SMR has been explored using different reactor configurations with dedicated solar concentration approaches (e.g., parabolic dish concentrators, solar towers, etc.) [1], economic viability has not yet been shown for any of them. Indeed, solar SMR remains costly because specialized concentration systems are necessary for existing reactor technology. Integrating SMR-capable devices to commercial concentrators, such as parabolic troughs, has therefore the potential to offer a cost-competitive solution for renewable hydrogen production. Compact reactors are however required in order to be located at the focus, without shading the incident sunlight. A micro-reactor was specifically developed by the authors for this application [2], as it integrates all the sub-processes necessary for an efficient SMR reaction, while being small enough to fit on the focal line.
of parabolic trough concentrators. This micro-reactor’s ability to produce hydrogen has notably been demonstrated in laboratory, by using a heating element to obtain the necessary temperature for a complete methane conversion rate. The work described here builds on those previous results, by presenting the reactor’s second-generation architecture, the manufacturing process of a prototype, and the results obtained under successful real-condition outdoor testing on a parabolic solar concentrator.

2. Solar Micro-Reactor Architecture
The micro-reactor developed for solar SMR is a highly integrated unit that fits directly on the focal line of parabolic trough concentrators, by stacking a linear array of micro-reactors units (Figure 1). Each one of these micro-reactor units is composed of a network of channels and chambers, which permit gas circulation and host a catalyst packed bed (Figure 2 b). The system’s sub-units are configured so that temperature decreases from the solar receiver on the lower hot side, to the upper cold side where the system’s inlets and exhaust are located. After entering one of the inlets, water is led to a nickel foam block, where vaporization occurs, allowing downstream gas mixing between vapor and methane. This gas mix is then heated in a counterflow heat exchanger, until it reaches the SMR main chamber where syngas is finally produced. The syngas obtained leaves the catalyst packed bed at a high temperature (~800°C), passing through the heat exchanger and losing heat to descending reagents. Further heat transfer is also made by conduction inside the micro-reactor’s walls, providing the needed energy for vaporization.

Although the developed architecture is compatible with low-cost manufacturing (e.g., stamping) and assembly (e.g., diffusion bonding), the micro-reactor block used for testing was manufactured with a 3D printing process (Figure 2 c), in order to accelerate prototyping. The following section presents further details about this prototype and the additive manufacturing process used.

3. Micro-Reactor Prototyping
The feasibility of the desired low-cost manufacturing process for the reactor has been previously demonstrated [2], and the developed demonstrator has therefore been manufactured using 3D printing (Figure 2 c), as the objective here is to show the system’s thermal and chemical capabilities. Precisely, the micro-reactor prototype is manufactured by Proto Labs with metal selective laser melting (SLM), also called direct metal laser sintering (DMLS). Stainless steel 316 had been selected for prototyping due to its good high-temperature and corrosion resistance. The resulting prototype comprises water and methane inlets, a syngas outlet, a vaporization zone, a heat exchanger, and an SMR packed bed (Figure 2). The absorptive surface has an area of 25.4 x 25.4 mm and is covered with a black coating Aremco HiE-Coat™ 840-MX, to increase radiation absorptivity.

The catalyst used is a Ni-Al spinel-based ~40 μm powder synthesized following the protocol developed by Abatzoglou et al. [3]. After the reactor’s core printing, filters are inserted into the reactor to prevent catalyst erosion (Figure 2 c). This catalyst is inserted using a hole that leads to an 80 mm³ SMR bed, included in the design before printing (catalyst inlet on Figure 2 c). To ensure complete filling of
the catalytic bed, vacuum is applied on the reactor’s exhaust and a small container with catalyst is set over the catalyst inlet. The catalyst is then aspirated in the cavity until the chamber is full. The filters prevent the catalyst from going farther in the reactor. The holes are then closed by welding small lids, resulting in a closed system. Other bores are also included in the structure to insert thermocouples all over the micro-reactor, allowing temperature measurements during testing. All the holes in the structure are further used to clear out the metal powder after printing. Three powder-exhaust holes, at the top of the reactor, are there for this single purpose, as they are closed before operation of the reactor.

Figure 2: a) Schematic of reactor architecture showing all the heat exchanges and fluid circulation, b) machined core of an elementary reactor showing the internal channel and chamber networks, and c) 3D printed micro-reactor prototype unit.

4. Experimental Test Bench
To perform solar reforming, the micro-reactor prototype has been mounted on the test bench shown in Figure 3. The global bench consists of a two-axis tracker and parabolic dish, with a surface of 0.37m² and focusing on the micro-reactor’s absorptive surface.

For testing purposes, the micro-reactor is contained in an aluminum chamber and insulated by a stack of silica wool sheets, preventing significant convection and radiation heat losses (Figure 3c). The chamber is fixed at the focus with aluminum arm and is chilled by liquid cooling (Figure 3b).

The chamber’s top lid includes all connection needed between the reactor and the control station. The first inlet allows gaseous reagents entrance for the whole duration of the test, while a second one exclusively provides liquid water. An outlet leads to a Drierite© desiccant packed bed and gas analyzers to collect and monitor the syngas produced by the reactor.

All the gas flows are controlled by MKS Instruments mass flow controllers, connected to a CompactRIO-9075 from National Instruments™ driven by a LabVIEW interface. A Harvard Apparatus Pump 11 Pico Plus Elite is used to precisely inject water in the system.

During the tests, the reactor is first heated by sunlight while inert gas (Ar) flows in the reactor to avoid catalyst coking. Once the reactor’s temperature exceeds 700°C, the argon flow is stopped and a mixture of CH₄ and CO₂ with a 1:1 ratio is delivered to activate the catalyst under dry methane reforming (DMR).
After a complete methane conversion is reached, the syringe pump injects a constant water flow while the CH4-CO2 mixture is changed for pure CH4 to perform SMR.

5. Test bench characterization

In this experimental campaign, the energy absorbed by the reactor was quantified by characterizing the off-the-shelf solar concentrator and absorbing coating that were used. First, a 25.4 x 24.5 x 6 mm stainless steel 316 plate, covered with the same black coating as the reactor, was made and equipped with a thermocouple. This plate was set in the insulated chamber and heated using the parabolic dish system of Figure 3. Once the system reached steady state at around 800°C, heating was stopped by turning the system off the sun. Knowing the thermal inertia of the plate, its registered temperature drop rate was used to calculate the heat loss rate, at a temperature of 800°C. In steady-state, the heat loss is equal to the heat absorbed by the plate, so it can be calculated using the following equation:

\[
Q_{abs} = Q_{loss} = m \cdot C \cdot \frac{dT}{dt}
\]

where \(m\) is the plate mass and \(C\) the material’s heat capacity.

Using this methodology, an absorbed power of 150 W was measured for steady state at 800 °C. When converted to radiation absorbed at the surface of the reactor, this corresponds to a power of 240 kW/m², which is a low value for such a high temperature application.

6. Results and Discussion

The experimental results obtained demonstrate the concept of methane reforming at low solar concentration with a micro-reactor. Indeed, complete methane conversion was observed at 800°C for a 50 SCCM methane flow under both steam and dry reforming, demonstrating the desired operation of the micro-reactor.

Only partial conversion was observed for a methane flow of 100 SCCM. This last result is however unexpected since a 100 SCCM methane flow represents a gas hourly space velocity (GHSV) of 7 500 ml/h*ml\(^{-1}\)cat, which is less than the value for near-complete conversion achieved in laboratory (GHSV of 35 000 ml/h*ml\(^{-1}\)cat), with the same catalyst [2]. Further tests will be performed on the reactor to evaluate the mismatch between predicted and measured conversion rates. Insulation system improvements will also be made to allow higher thermal efficiency. These improvements comprise the use of a better solar-selective coating, the addition of solar glazing in front of the reactor, and the use of a vacuum system to avoid convection around the reactor.

7. Conclusion

This paper presented the design and real-condition testing of a new prototype of solar micro-reactor for natural gas reforming. The prototype was made using additive manufacturing, which allows easy integration of all sub-processes required to perform dry and steam methane reforming. A complete conversion of methane to syngas has been performed, while operating the micro-reactor at 800°C, with a CH\(_4\) flow of 50 SCCM and absorbed sunlight corresponding to 240 suns. The results obtained confirm the feasibility of methane reforming at a moderate solar concentration, characteristic of low-cost solar concentration systems.

References

[1] Agrafiotis, Christos, Henrik von Storch, Martin Roeb, and Christian Sattler. « Solar Thermal Reforming of Methane Feedstocks for Hydrogen and Syngas Production—A Review ». Renewable and Sustainable Energy Reviews 29 (janvier 2014): 656-82.

[2] J-F. Dufault, I. E. Achouri, N. Abatzoglou, N. Baridy, L. G Fréchette and M. Picard. « Fabrication and Demonstration of Planar Micro-Reactors for Solar Steam Methane Reforming ». Journal of Physics: Conference Series 1052 (juillet 2018): 012055.

[3] N. Abatzoglou, J. Blanchard, and I. E. Achouri, “A Novel Ni-Al Spinel-Based Catalyst for Dry Reforming of CH4-Rich Gasification Tail Gas Streams,” presented at the 22nd European Biomass Conference and Exhibition, Hamburg, Germany, 2014, pp. 1004–1007.