Fabrication and Demonstration of Planar Micro-Reactors for Solar Steam Methane Reforming

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Abstract. This paper presents a novel solar micro-reactor architecture for cheap hydrogen production by methane reforming. Using microfabrication techniques to create three-dimensional channel networks in diffusion-bonded plates, all the sub-processes required for methane reforming are integrated in a small unit, which is well suited for implementation on cheap and well-established solar parabolic troughs. Monolithic integration of the sub-processes allows heat recovery from the high temperature reaction to the lower temperature endothermic processes such as water vaporization and reagent preheating. To demonstrate the manufacturing feasibility as well as the sufficient catalytic activity, a 4.5W stainless steel demonstrator is built and tested in the laboratory. Results show a complete methane conversion for temperatures over 850°C at a space velocity of 35 000 ml/h*ml_cat.

1. Introduction
If produced from clean sources, hydrogen could become excellent energy carrier in the future. However, today’s hydrogen mainly comes from fossil fuels. In particular, nearly 95% of the hydrogen produced currently comes from standard steam methane reforming (SMR) plants [5]. Within these plants, steam is added to methane and heated between 800 and 1000°C [6] to engage the catalytic SMR reaction:

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H = 206 \text{ kJ/mol} \quad (1)$$

For hydrogen production purposes, the residual carbon monoxide is further oxidized in the mildly exothermic water gas shift reaction (WGS) to increase the hydrogen release per unit of CH₄:

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{ kJ/mol} \quad (2)$$

Within the SMR reactor, both reactions 1 and 2 can occur at the same time, leading to the creation of CO₂ even before the WGS reactor. The global reaction is endothermic and is represented by:

$$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \quad \Delta H = 165 \text{ kJ/mol} \quad (3)$$

The ratio between the released CO and CO₂ is stated by the thermodynamic equilibrium which mainly depends on temperature, pressure and steam to carbon ratio (S/C). However, even if it is the thermodynamic equilibrium that states the final concentrations, catalyst must be used to accelerate the reaction for commercial applications.

In conventional power plants, the energy necessary to complete the reaction comes from burning part of the natural gas feedstock. Consequently, a substantial feedstock saving can be achieved if the heat addition comes from a renewable source. That may results in costs reductions, as feedstock represents the biggest part of the hydrogen levelized cost of energy (LCOE) in conventional SMR plants [9].
Solar energy is the source of renewable energy typically considered for SMR as it is an abundant resource and can satisfy the high temperature required for the SMR reaction when concentrated [6]. Common solar concentrators considered for this application are parabolic dishes (PD) and solar towers (ST), which are well suited for high temperature applications since they can provide high solar concentration [6], [16]. On the other hand, conventional parabolic trough (PT) concentrators are cheap and commercially established, but come with lower concentration capability, which constitute a great challenge for solar-aided SMR. Consequently, there is no report of a successful implementation of an SMR reactor directly on the focal line of a parabolic trough. Moreover, no exhaustive studies on the feasibility, efficiency and interest to implement such a technology at high temperature seems to appear in the literature despite the several advantages that it could represent. Part of the challenge with this approach is in fitting the reactor along the narrow focal line of a parabolic trough. This paper presents a new design of a fully-integrated solar micro-reactor capable of processing the entire SMR reaction at low solar concentration in an inch-wide unit. The micro-fabricated reactors can be stacked in thin arrays to cover the focal line of a parabolic trough. Taking advantage of the synergy between the endothermic and exothermic processes, the highly-integrated design redirects thermal losses from the high temperatures zones to satisfy the energy requirements of the lower temperature sub-processes, such as water vaporization and reagents preheating. A prototype is tested in the laboratory using a heating element to demonstrate chemical performance of the systems as well as its manufacturing feasibility. More precisely, the reactor shows a complete SMR reaction of methane at 850 °C and 900 °C for gas hourly space velocities of 35 000 and 70 000 SCCM/h*mlcat, respectively.

2. Architecture
In this concept, elementary planar reactors are made of 2.5D metallic plates containing all the endothermic and exothermic sub-units required to complete the reforming process (Figure 1). The micro-reactors are then stacked and diffusion-bonded in parallel in the axis of the PT to form a monolithic unit at the focus line of the concentrator. Using this two-dimensional approach, layers can be manufactured by a standard batch process such as etching, punching and laser cutting. These manufacturing methods are compatible with a high volume production economy, instead of a scale economy typical to solar towers. The sub-units of the elementary reactors are placed so that the temperature increases linearly from the inlet on the cold side to the solar receiver on the hot side (Figure 1-a). First, water enters the central inlet and passes through nickel foam where it evaporates (Figure 1-b). This steam then flows to the heat exchanger entrance where it mixes with the methane flow. It then gradually heats up in the counter flow heat exchanger and flows into the SMR sub-reactor. The reformed gas then leaves the packed bed at a high temperature and releases its heat to the reactant mix and evaporating water, before it is exhausted. The remaining energy needed to vaporize water comes from the conduction inside the reactor’s walls.

![Figure 1](image1.png)

**Figure 1:** a) Schematic of the demonstration elementary reactor’s core, b) Machined core of the demonstration elementary reactor.

3. Prototype
The core of this elementary reactor prototype is micro-machined in a 1.2 x 25 x 50 mm stainless steel 316 sheet (Figure 1). For the demonstration purpose, stainless steel 316 is used due to its good resistance to
corrosion as well as its known properties and easy machining. The reactor is closed by a 0.004" thick SS-316 layer joined by diffusion bonding at 750°C for 90 minutes under a nitrogen atmosphere and an initial load of 50 MPa. The intermediate 0.005"-thick nickel foil shown on Figure 2 only acts as an interlayer to facilitate the diffusion bonding with no other structural function. All the faces were polished with a 1 µm suspension to facilitate bonding and increase tightness. A Ni-Al spinel-based catalyst is used to perform the SMR reaction and is synthesized using the protocol developed by Abatzoglou [4]. First, a nickel 40 µm alumina powder (#43266 from Alfa Aesar) is mixed with water. Five percent of nickel (m/m) is then added to the alumina powder using an aqueous solution of Ni(NO₃)₂*6H₂O. After 90 min of stirring at 60°C, the mixture is heated up to 95°C under mixing until the water is evaporated. The impregnated powder is then dried at 105°C for 12 hours. Finally, the powder is calcined for 6 hours at 900 °C under atmospheric pressure to reach the desired spinel-phased catalyst. Since the catalyst can sustain high temperatures, it is inserted inside the reactor before the diffusion bonding.

4. Experiments
The test bench shown in Figure 3 is used to perform the tests. A first inlet provides the gas needed for the entire duration of the cycle and a second acts exclusively as a liquid water inlet. A third manifold collects the synthesis gas and brings it to the analysis system. A custom-made heating element is wrapped around the reactor base to provide the high temperature needed for the reaction to occur. A standard PID system using the feedback provided by a thermocouple controls the heating element’s temperature. A CPU liquid cooling system chills the reactor’s head and protects the manifold gaskets during the system ramp-up and the catalyst activation. The gas flows are controlled using three flow meters (Alicat) controlled with a LabVIEW interface. The first cylinder provides argon needed during the reactor’s heating and cooling. The second cylinder contains a stoichiometric mixture of CO₂ and CH₄ needed to activate the catalyst and the third contains pure CH₄ for standard reactor operation. Once the synthesis gas escapes the reactor, it passes through a cooling coil submerged in an ice bucket and a separator to condense the unprocessed water. The gas then passes in a Drierite© packed bed for final drying. A mass spectrometer placed downstream continuously monitors the exhaust composition changes while gas is sampled and precisely analyzed using a Varian 3800 Micro GC. During the tests, the reactor is first heated from room temperature to 950°C. The ramp up lasts about 8 min and only argon is injected in the reactor to avoid carbon deposition. The argon stream is then switched to a 1:1 CH₄:CO₂ stream to activate the catalyst under dry methane reforming conditions (DMR). When a complete conversion of methane is observed, water is injected in the reactor using a syringe pump (Harvard Apparatus 11 Pico Plus Elite) at a steam to methane ratio of 1:1. The change in CO₂ concentration observed by the mass spectrometer corresponds to water appearing in the reactor. At this point, the CH₄:CO₂ stream is changed for pure CH₄ and the water flow is increased to achieve a steam to carbon ratio of 2:1. The temperature is then reduced by increments of 50 °C until it reaches 650°C. For each temperature step, composition of the gas produced is analyzed with the gas chromatograph. Two sets of experiments corresponding to different mass flows are performed during the tests. The first one corresponds to a gas hourly space velocity (GHSV) of 35 000 ml/h*mlcat at standard temperature and pressure, which represents a power conversion of 75 suns under a complete sun to chemical energy conversion. The second set of data is taken at a GHSV twice as large, i.e. 70 000 ml/h*mlcat. A steam to carbon ratio of 2:1 is used for all the experiments.

5. Results
Figure 4 shows the methane conversion level achieved during the experiments. Complete methane conversion occurred for temperatures over 850° at low GHSV, and over 900° under high GHSV. At low GHSV and temperatures higher than 750°C, the conversion is close to thermodynamic equilibrium. As the temperature decreases, the conversion departs from equilibrium with conversion 30% lower than the equilibrium at 650°C for low GHSV. At high GHSV the conversion level departs dramatically from equilibrium under 850°C and becomes as low as 26% at 650°C. The complete
methane conversion speaks to the fact that the H$_2$O-CH$_4$ mixing length between the evaporator and the catalyst is sufficient to provide a homogenous mix to the SMR reactor.

Three cycles were performed with this first demonstrator and no leak was detected during 20 h of operation. In addition to the high conversion level reached for SMR, these tests have also shown that dry methane reforming as well as mixed steam-CO$_2$ reforming with a complete methane conversion are achievable at 950°C and even colder.

It also shows the potential of the manufacturing process although further analysis must be done to determine the unit’s resistance to degradation. Finally, it partly demonstrates the principle of integrating multiple sub-reactions and recuperating waste heat, underlying micro reactor concept and suggesting that the heat recovery is indeed implementable in such compact integrated units.

6. Conclusion

This paper presents a new design of solar micro-reactor for steam methane reforming. Using an integrated design, the system comprises all the necessary components to fulfil hydrogen generation with SMR. With each of these components being thermally coupled, this synergy allows reusing heat from the warmer processes to fulfil the energy requirement of the colder processes such as water vaporization and reagent preheating. A layered configuration was developed based on laminated metal sheets, compatible with eventual cost-effective batch manufacturing. A micro-reactor demonstrator was fabricated to demonstrate the reactor feasibility and its reforming capabilities, as well as validate its integrated layout and layered fabrication approach with catalyst integration. The tests made at 35 000 and 70 000 ml/h*mlcat show a complete methane conversion level above 850 and 900°C, respectively. For the lowest GHSV, the methane conversion stays close to the equilibrium concentration until the temperature falls under 750°C. The reactor also resists to the strong temperature gradient and is able to complete water vaporization as well as reagent mixing inside the compact volume, which shows the feasibility of the laminated integrated elementary reactor for eventual operation in parallel.

References
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