



# Structured Catalysts for Methane Auto-Thermal Reforming in a Compact Thermal Integrated ATR Reformer

Vincenzo Palma<sup>a</sup>, Antonio Ricca<sup>\*a</sup>, Paolo Ciambelli<sup>a</sup>

<sup>a</sup>Department of Industrial Engineering, University of Salerno, via Ponte Don Melillo, 84084 Fisciano (SA), Italy  
[aricca@unisa.it](mailto:aricca@unisa.it)

Hydrogen and fuel cells combination is the most viable answer to the antithetic problems of growing energy demand and environmental pollution reduction. Due to the well note difficulties in H<sub>2</sub> transport and storage, distributed H<sub>2</sub> production results the most promising solution, so very compact and small size production plants are required. To this goal, hydrocarbons ATR reaction assures a self-sustaining process and high reactor compactness, resulting as the best method for distributed H<sub>2</sub> production to couple to a fuel cell system. In spite of the increasing interest in renewable sources, due to the low costs and the widespread existing delivery pipelines, fossil fuels reforming still remain the best choice in a transition period towards hydrogen based economy.

In this work a compact catalytic reactor was analyzed for the ATR of CH<sub>4</sub> as natural gas surrogate. Structured catalysts (commercial honeycomb and foam monoliths) performances in CH<sub>4</sub> processing were studied. In reactor design, great attention has been paid to the thermal integration, in order to obtain a total self-sustainability of the process avoiding additional external heat sources, and improve the plant compactness. Through an heat exchange system integrated in the reactor, water and air stream are preheated by exploiting the heat from exhaust stream, allowing to feed reactants at room temperature as well as cooling product stream at a temperature suitable for further purification stages (WGS, PROX). In order to have a very comprehensive process analysis, temperatures and composition were monitored in 6 point along the catalytic bed. The influence of catalytic system geometry as well as thermal conductivity in the process performances was also analysed. Preliminary tests showed high thermal system efficiency, with a good hydrocarbon conversion at different operating conditions for both catalyst typologies.

## 1. Introduction

In the last years the interest of energy world toward fuel cells has quickly grown, due to the influence of the green global economy. The polymeric electrolyte membrane fuel cell (PEM) appears as the most advanced technology, due to their very low size and high speed conversion especially when hydrogen is used as feed. The PEM cells are very light and have a specific power higher than other fuel cells; so, they are the best candidate for possible on-board applications. Therefore the interest in hydrocarbons distributed fuel processing is growing in energy industry world. In particular, methane (CH<sub>4</sub>) is the most used hydrocarbon, due to its highest H/C ratio, as well as its easily availability. The aim of a fuel processor is to convert hydrocarbons in a H<sub>2</sub>-rich stream to feed a fuel cells system. Three main steps are involved: the reforming process, in which syngas is obtained from hydrocarbon; the water-gas-shift

(WGS), in which CO present in syngas is converted in further H<sub>2</sub>; the preferential oxidation (PROX), in which the remaining CO was eliminated by selective oxidation.

In principle, ATR may be considered as the sequence of Partial Oxidation (POX) and Steam Reforming (SR) reactions (Scognamiglio, et al., 2012): the oxidative reaction occurs as a first step of the process, while the steam reforming reaction starts when the process steam reaches a consistent temperature. It is a self-sustained catalytic process, in which the exothermicity of hydrocarbon oxidation reaction supplies to the system the heat needed for the endothermic SR reaction; therefore, as a typical ATR reactor behaviour, along the catalytic bed the temperature quickly raises the first zone, and then slowly decreases until the end. Exothermicity of the reaction as well as hydrogen yield depend strictly on feed ratio values  $x$  and  $y$ . Auto-thermal operation point is the condition at which the energy requirements of the SR reaction are balanced by oxidation reactions (Haynes and Shekhawat, 2011). By aiming to achieve a distributed H<sub>2</sub> production, simple, very compact and versatile systems, characterized by fast start-up time and very quick response to feed changes are required. To this goal, the chemical characteristics of ATR reaction, like high reaction rate, and the absence of external heat sources, candidate the ATR of hydrocarbons as one of the most promising selections (Ciambelli, et al., 2009). Since ATR reaction involves 3 different reactants, both liquid and gaseous, the proper reactants mixing results a basic prerequisite in order to achieve high yield and selectivity toward desired products, avoiding coke formation and catalyst deactivation (Aasberg-Petersen, et al., 2011).

Despite ATR is a thermally self-sustained process, reactants temperature at the inlet section of the catalytic bed influences the thermal profile along catalyst, the outlet temperature and then the fuel conversion and the H<sub>2</sub> yield (Zahedi nezhad, et al., 2009; Ding and Chan, 2008). Higher reactants temperature assures higher hydrocarbons conversion. On the other side, products temperature was about 700-800 °C, while further purification stages, like Water Gas Shift (WGS) and CO Preferential Oxidation (PROX) need lower temperature, respectively about 300 °C and about 100 °C (Kim, et al., 2010; Hwang, et al., 2011; Sirichaiprasert, et al., 2008; Laguna, et al., 2011; Sekhavatjou, et al., 2011). In order to reduce plant size and operating costs, very advantages may be achieved by heat transferring from products stream to fed streams (Qi, et al., 2007).

In ATR process, the choice and the optimal setup of the catalytic system play a fundamental role in the plant design. Catalyst selection may greatly affect both the conversion degree and the selectivity of the reaction, so the presence of an active species rather than another one can lead to different reaction products. Obviously, the catalyst selection should be made according to the defined operating conditions and based on the selected fuels. Since the ATR process may be considered as the synthesis of SR and POX (Chen, et al., 2010), the catalyst must ensure simultaneously a high selectivity towards these two reactions, inhibiting other unwanted, such as hydrocarbon cracking. Several studies have demonstrated that nickel (Mosayebi, et al., 2012; Rezaei, et al., 2011; Hoang and Chan, 2007) as well as noble metals (Pt, Rh, Ru) (Li, et al., 2011; Qi, et al., 2007) supported on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> or ZrO<sub>2</sub> show good activity toward reforming reactions (Souza and Schmal, 2005; Cai, et al., 2008; Yuan, et al., 2009; Lisboa, et al., 2011); improvements in stability and selectivity are achieved from bimetallic catalytic systems (Cimino, et al., 2010). Great attention must be also devoted to the catalyst structure (e.g. powder, pellets, honeycomb, foams, etc.) (Liu, et al., 2004). Previous studies have demonstrated that high thermal conductivity supports allow a flat thermal profile along catalytic bed (Palma, et al., 2009), and thus a higher outside temperature of products that leads at higher hydrocarbon conversion (Halabi, et al., 2011). In this way, metal based honeycomb and foams monoliths are selected as very promising supports for ATR catalytic systems (Ciambelli, et al., 2010). Furthermore, such supports minimize pressure drops along catalytic bed. In this works preliminary tests were performed on a catalytic ATR reformer thermally integrated to investigate the catalytic performances of two monolithic catalysts, with honeycomb and foam structure.

## 2. Experimental

A catalytic auto-thermal reformer was designed and realized, to produce up to 10 Nm<sup>3</sup>/h of H<sub>2</sub> by methane processing. In the reaction system a thermal recovery module was integrated, aimed to preheat reactants by exploiting sensible heat from exhaust products stream: so a self-sustained system was obtained, and no external heat sources are needed (Palma, et al., 2011).

In experimental tests, air (as oxidant gas), bi-distilled water and methane (as surrogate of natural gas) were used. Methane (purity of 99.95 %) and air (ultrapure, 99.998 %), both supplied from SOL spa, were delivered to the system by means of thermal mass flow controllers (Brooks Instruments); bi-distilled water was stocked in a 7 atm pressurized vessel, and delivered to the system by means of a Coriolis based mass flow controller (Quantim, Brooks Instruments). Air and liquid water were delivered to the heat exchange module for pre-heating procedure, and then hot air and super-heated steam were inserted in mixing module. CH<sub>4</sub> was fed directly in the mixing module, without any heating procedure, in order to avoid fuel cracking. The special shape of mixing module, characterized by a series of section expansions and restrictions, allows the formation of eddies and whirlpool, so realizing a very effective reactant mixing that assure an uniform temperature and composition at the end of the module.

The catalytic module, realized in stainless steel AISI 310 with a rectangular section (sized 60 x 80 mm), is placed just after the mixing zone. Its particular shape assures an easy access to the catalytic volume, so facilitating the catalyst replacement procedure. The start-up phases are assisted by an electrical resistance (trigger) located just before the catalytic bed. In the catalytic volume, a series of 6 thermocouples and sampling tubes are placed with a distance of 14 mm between them: so a very comprehensive reaction trend analysis was achieved along the whole catalytic bed. The sampling lines are provided to a mass spectrometer; by means of a Proteus multivalve, it's possible to have a simultaneous monitoring in the different zones of the catalytic volume.

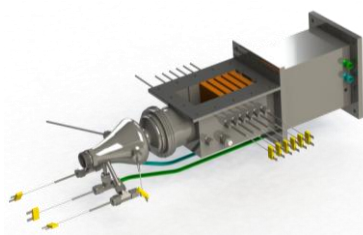


Figure 1: Integrated ATR reactor

Two different catalysts were used in our tests: in a first time a commercial honeycomb noble metals based monolithic catalyst (provided by BASF<sup>®</sup>, 400 cpsi) was used. It's divided in 5 bricks each sized L 27 x H 36 x W 11 mm, for a total catalytic volume do 55 cm<sup>3</sup>; the bricks are placed at 3 mm between them, in order to assure a stream mixing along the catalytic bed. By this configuration, gas temperature and composition could be measured after each brick. In a second time a commercial foam monolith (noble metals based, deposited on Al<sub>2</sub>O<sub>3</sub> 65 ppi foam, provided by JM<sup>®</sup>). It's composed by 5 foam disks sized D 29 x W 15 mm, attached between them to obtain a cylindrical shape sized D 29 x W 75 mm, for a total catalytic volume of 50 cm<sup>3</sup>. The experimental tests were performed by feeding to the system air, water and methane by fixing the feed ratio (H<sub>2</sub>O:O<sub>2</sub>:C = 0.49:0.56:1) and the space velocity (GHSV = 120,000 h<sup>-1</sup>). The gas composition obtained in each point of catalytic bed is compared to thermodynamic equilibrium values, calculated by GasEq software (a Windows freeware software based on the minimization of Gibbs free energy) (Morley, s.d.) as an isotherm reaction at the corresponding temperature and pressure.

### 3. Results

#### 3.1 Honeycomb monolith catalyst

The honeycomb monolith bricks, placed at a distance of 3 mm between them, are wrapped in an insulating material (thickness 1.7-2.2 mm) in order to avoid by-pass phenomena and to achieve an adiabatic reaction. The activity tests are performed by holding reactant feed ration (H<sub>2</sub>O:O<sub>2</sub>:C = 0.49:0.56:1) and space velocity (GHSV = 120,000 h<sup>-1</sup>). The products composition and methane conversion profile along the catalytic bed is reported in Figure 2a, while temperature profile is reported in Figure 2b. As a results, the reaction take place mainly in the first part of the catalytic bed, as after the first catalytic block, hydrogen content and methane conversion are within 80 % of the final value.

At the end of catalytic bed the products stream composition appears very close to the thermodynamic equilibrium: this result attests a relevant activity of the investigated catalyst also a higher GHSV value. At the same time, a very high methane conversion was obtained in the tests: the X<sub>CH<sub>4</sub></sub> increases constantly after each brick; however outside the last brick the thermodynamic equilibrium value is reached, so no further increasing was expected.

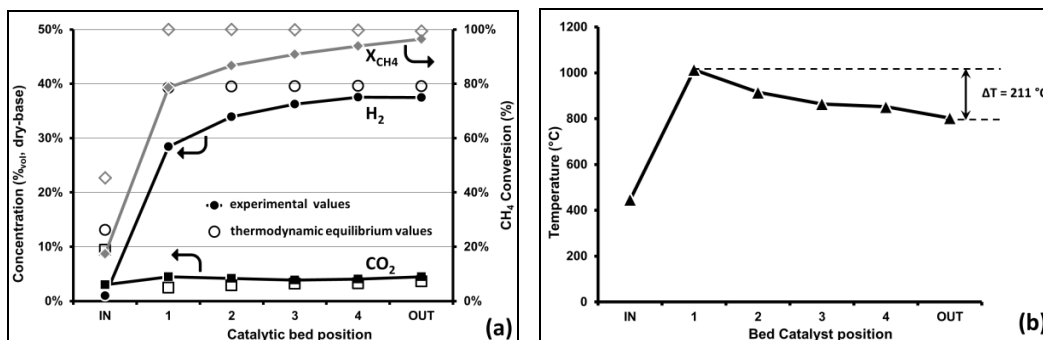


Figure 2: Reaction stream (a) composition, (b) temperature profiles along the honeycomb catalytic bed

In Figure 2b the temperature profile along the catalytic bed is reported. As expected, the temperature quickly raises in the first zone of the catalyst, in which the exothermic reactions (methane partial or total oxidation) take place, and then slowly decrease due to endothermic steam reforming reaction.

### 3.2 Foam monolith catalyst

The foam cylinder is placed in an insulating brick sized 60 x 80 x 75 mm in order to reduce heat loss in catalytic volume. The activity tests are performed in the same feed condition of previous catalyst. In the Figure 3a the composition profile along the catalytic bed is reported.

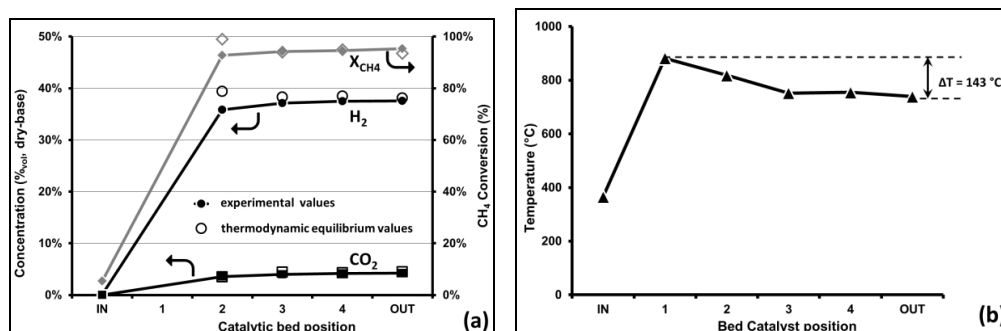


Figure 3: Reaction stream composition (a) and temperature (b) profiles along the foam catalytic bed

The composition and conversion profiles clearly shows that the reaction may be considered concluded just after the 2<sup>nd</sup> catalytic disk: the products stream composition seems very close to thermodynamic equilibrium in every points of catalytic bed. The analysis of thermal profiles (Figure 3b) underlines that just after the 3<sup>rd</sup> foam disk no relevant temperature changes were recorded, and according to the composition behavior along the catalytic bed, the ATR reaction mainly occurs in the first 3 disks.

By comparing system performances of monolith and foam catalysts (Figure 4) it's easy to note that no relevant differences are founded: the highest temperatures in honeycomb catalyst may be considered as a consequence of an higher inlet temperature in catalytic bed, due to a better performance of heat recovery module: so in the honeycomb catalyst a higher methane conversion was recorded. Finally, a flatter temperature profile was observed in foam catalyst: the continuous structure of the foam allows a better conductive heat exchanger along the catalyst, so the temperature peak is distributed along the whole catalytic bed, obtaining a weak temperature increase in output section.

## 4. Conclusions

An ATR reaction system thermally integrated was set-up for catalytic activity screening, with a multipoint stream analysis to monitor the composition and temperature in several points of catalytic bed. The activity tests were performed for two commercial monolithic catalysts noble metals based, one honeycomb supplied by BASF configured as 5 separated bricks, and one monolithic foam supplied by JM. The tests results evidenced the very high activity of both catalytic systems, that quickly reached

the equilibrium values. The influence of the stream mixing is underlined by comparing composition profiles of the two different configurations: in the foam catalyst, in which an optimal stream mixing is realized, the composition profile is flatter than in the honeycomb. The foam catalyst was even characterized to a flatter thermal profile, due to the better conductive heat along the one-piece catalytic monolith. On the other side, the best overall performances observed in the honeycomb monolith underlines the influence of the input gas temperature, that leads to an higher thermal profile and then higher hydrocarbon conversion. In this way, the thermal insulation of catalytic area should cover a crucial role on ATR system setup. Further investigations may be conducted on higher space velocities, as well as on higher steam-to-carbon ratio, in order to test the catalyst activity in higher stress conditions.

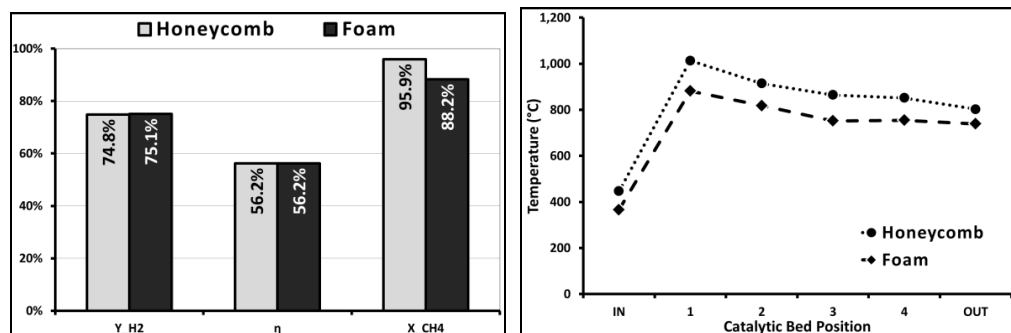


Figure 4: Performances key features and temperature profiles comparison between honeycomb and foam monolithic catalysts

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