Energy sustainable development through methane autothermal reforming for hydrogen production

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The peculiar characteristics of CH_4 catalytic autothermal reforming make this process a good candidate for a hydrogen based distributed power generation. The feasibility of this option is closely linked to both technological and economical aspects. Indeed, the choice of a very highly active catalyst to reach the goal of reactor compactness as well as the costs comparison of small scale plants with that of large scale ones are essential requirement to assess the suitability of the former for an energy sustainable development. In this paper the performances of ATR structured catalysts in form of monoliths or ceramic foams are compared. Moreover, the production costs of a traditional scheme (ATR+PSA) for a 50 m^3/h (STP) small scale unit are reported. Such a scheme could be applied to natural gas fed stationary plants.

1. Introduction

A distributed energy system is an efficient, reliable and environmentally friend alternative to the usual energy systems. In a distributed power generation system the energy conversion units are situated close to energy consumers, and large units are substituted by smaller ones thus providing that single buildings can be completely self-supporting in terms of electricity, heat, and cooling energy (Alanne and Saari, 2006). In particular, concerns regarding national security, emissions of greenhouse gases, finite sources of fossil fuels, and environmental quality are partially or wholly resolved if hydrogen energy systems are employed (Dixon, 2007). Indeed, the versatility of hydrogen as a fuel is represented by the multiple feedstocks from which it can be derived, including fossil fuels, biomass and water (Turner, 2004). However, though the technologies for hydrogen production, storage and distribution exist, they need to be adapted for use in an energy system since building a new hydrogen energy infrastructure would be expensive and involves logistical problems in matching supply and demand during the transition period. From the economical point of view, in spite of the high production costs which characterize the small-scale hydrogen plants when compared with that of the well established large scale plants, the delivered cost at the point of consumption of the former may become competitive. Among the common technologies, the peculiar characteristics of autothermal reforming reaction (ATR) make this process a good candidate for a sustainable distributed hydrogen production. In particular, a methane ATR reactor when compared with a steam reformer, is characterized by higher simplicity and compactness, therefore it is less costly to build. However, a very active catalyst and an optimal geometry are required for the reactor design and to achieve high methane conversion. From this point of view, a structured catalyst can operate at significantly higher space velocities than pellets catalyst thus providing both a reduction of reactor size, weight and cost and more rapid thermal

responses to transient behaviour (Giroux et al., 2005). With regards to catalyst active species, noble metals based catalysts have been widely investigated for either methane and diesel autothermal reforming reaction (Souza and Schmal, 2005; Cheekatamarla and Lane, 2005a, 2005b, 2006). A medium term innovative option to enhance the H_2 yield is the integration of the ATR reactor with a membrane for hydrogen separation which should allow a higher CH_4 conversion even at low temperatures by continuous H_2 removal (Kikuchi, 2000). However, the feasibility of such integration is strictly correlated to the temperature profile established along the catalytic bed as too high temperatures (> 600°C) could irreversibly damage the membrane (Tiemersma, 2006). Previously, Ciambelli et al. (2005) reported on the development and optimization of a thermally self sustained ATR reactor by heat integration of the air and water fed to the reactor by the hot exhaust stream. Furthermore, the reactor was employed to carry out catalytic activity tests at high space velocity ($45,000 \text{ h}^{-1} < \text{GHSV} < 90,000 \text{ h}^{-1}$) with a noble metals catalysed honeycomb monolith (Iaquaniello et al., *submitted*) showing that such a catalyst is enough active to provide a CH_4 conversion and a product distribution close to the equilibrium values.

In this work we report results of ATR catalytic activity tests carried out on both noble metals based structured monolith and cellular foam catalysts. Experimental tests are performed at different operating conditions in order to reach inside the reactor temperature values more suitable to integrate a membrane for hydrogen separation. In addition, in a more traditional approach, the production costs of the ATR+PSA scheme for a 50 m^3/h (STP) unit have been developed.

2. Experimental

A schematic picture of the thermally ATR self sustained stainless-steel reactor (36 mm i.d.) is reported in Figure 1. It consists of a lower section where, only during the start-up phase, does methane react with air at a fixed O_2/CH_4 ratio and an upper catalytic section where reforming reactions occur. In the start-up phase the heat released in the lower section is transferred to the reforming section heating the catalytic bed up to the ATR catalyst threshold temperature. Methane and air are fed at the bottom of the reactor in a mixing chamber at the exit of which a SiC foam is placed to obtain a well distributed and homogeneous flame. In the reforming section, the catalyst bed is supported by a metallic gauze at the bottom of which water is fed to the reactor. The reactor is integrated with two heat exchangers to

Figure 1. *Schematic picture of ATR reactor*

preheat the air and the water by the hot exhaust stream. Three thermocouples (TrefL, TrefM, TrefH), located respectively at 25%, 50% and 75% of the catalytic bed height, provide the temperature profile in the reactor's axial direction. A differential pressure sensor monitors the pressure drop across the reactor. The outside shell of the reactor is thermally insulated to reduce heat loss. A constant flow of exhaust stream is sent to the analysis section through a 0°C cold trap. Reactor start-up is performed by feeding a water-free mixture of methane and air with a molar O_2/CH_4 ratio of 1.36 and by inducing for few seconds a voltaic arc between two spark plugs placed on the surface of the SiC foam. After that, water is fed to the reactor and the O_2/CH_4 (x) and H_2O/CH_4 (y)
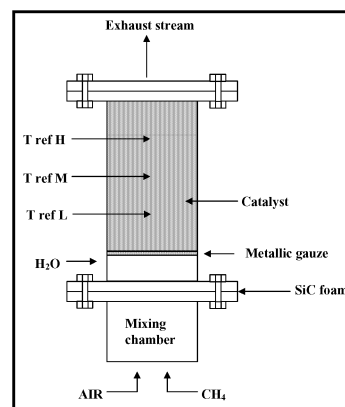
ratios are varied to the desired values. In this work the following range of operating conditions was adopted:

$$0.25<x< 0.60; \ 0.49<y <2.0; \ 12,000 \ h^{-1}<GHSV<47,000 \ h^{-1}$$

Two differently structured catalysts based on noble metals were employed for catalytic activity tests. The former is a honeycomb monolith (ATR7B, Engelhard Corporation, Figure 2a), the latter was obtained by deposition of the same catalytic washcoat on a 6 ppi SiC foam (Figure 2b).
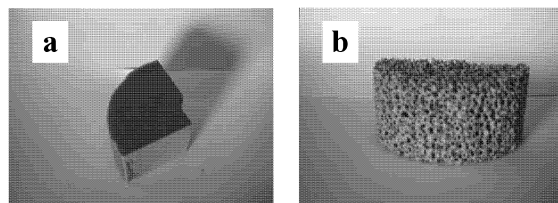

Figure 2. *Noble metals based ceramic monolith catalyst (a) and SiC foam catalyst (b)*

3. Results and discussion

In Figure 3 the temperature profiles along the catalytic bed, the product distribution, experimental and equilibrium CH_4 conversion (evaluated at TrefH) obtained for the monolith catalyst are reported. Results show that the temperature profile along the catalytic bed is characterized by a higher temperature in the low zone of the reforming section followed by a temperature decrease in the medium and high zone of the catalytic bed. Only for the O_2/CH_4 equal to 0.25 a change in the temperature profile occurs, characterized by higher temperature in the medium zone of the catalyst bed with respect to the low zone. With exception of the test performed at x=0.25, all the results show that TrefL values are higher than 700°C. In particular, the temperature profiles appear more uniform by decreasing the GHSV value and by increasing the y value. In the three tests carried out at x=0.60, CH_4 conversion and H_2 concentration are very close to the equilibrium values. In Figure 4 the temperature profiles along the catalytic bed, the product distribution, experimental and equilibrium CH_4 conversion (evaluated at TrefH) obtained with the foam catalyst are reported. A similar profile was found with ceramic foam. The highest temperature of 795°C is relevant to the test performed at 25,000 h^{-1} with O_2/CH_4 and H_2O/CH_4 feed ratios equal respectively to 0.6 and 1.0. For all the tests carried out at 12,000 h^{-1} lower temperature values are observed. In particular the maximum TrefL value is around 600°C. Moreover a reduced temperature gradient along the catalytic bed is obtained. It is worth to know that at each operating condition both CH_4 conversion and H_2 concentration are very close to the expected one from thermodynamic evaluation, especially in the tests performed at higher contact time.

In spite of the low O_2/CH_4 and H_2O/CH_4 feed ratios employed in the reported catalytic activity tests, no coke formation was noticed for the entire test duration (Figure 5) as confirmed by the pressure drop constant signal.
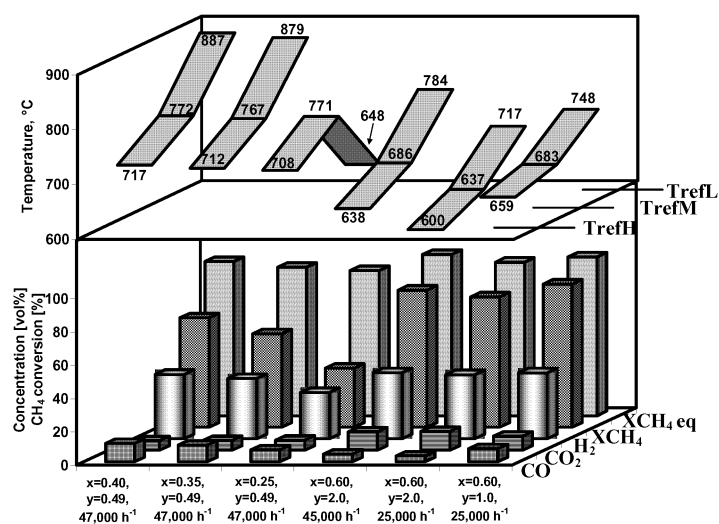
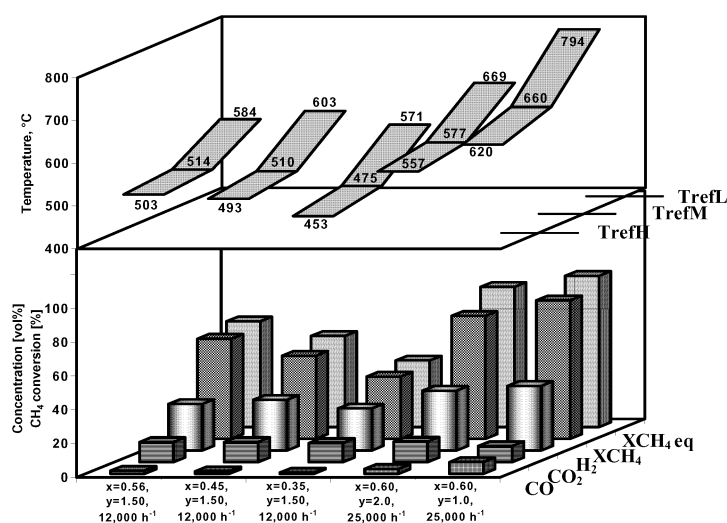**Figure 3.** *Temperature profile, CH_4 conversion and product distribution with monolith catalyst*

Figure 4. *Temperature profile, CH_4 conversion and product distribution with foam catalyst*
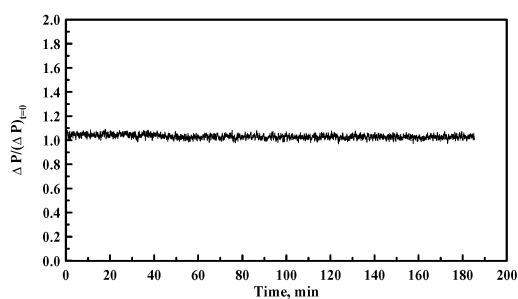

Figure 5. *Pressure drop during catalytic activity test with foam catalyst*

4. Costs estimation

An economic evaluation was carried out for a traditional scheme ATR+PSA for H_2 production taking into account the variable operating costs, the investment costs and the rate of depreciation. Our cost analysis was kept quite simple, the main target being to simply evaluate the overall production costs. In Table 1 the basic economic assumptions and parameters are reported.

Table 1. *Basic economic assumption and parameters*

Parameter	Basic assumption
Natural gas price	0.18 E/ m^3(STP) (LHV= 8700 Kcal /m^3(STP))
Electricity price	0.085 E/kWh
Cooling water price	0.07 E/ m^3
Capacity factor	80% at design capacity
H_2 Plant capacity	50 m^3/h (STP)
Depreciation	10%/ y of investment
Maintenance materials & labor (H_2 section)	2,5% of the investment

For the evaluation of the variable operating costs, which include the consumption of feed+ fuel, cooling water and electricity, it was taken into account that under the actual economic scenario the costs for such a scheme are mainly related to those of the natural gas and of the plant thermal efficiency. The evaluation is reported in Table 2.

Table 2. *Variable costs estimation*

	Feed + fuel	Water	Electricity	Overall cost
Specific consumption	4850 kcal/m^3(STP)	0.03	0.35 kWh/m^3(STP)	
Specific costs	0.10	0.002	0.03	0.132

The investments are estimated on the basis of a long-term experience in building hydrogen production plants and on the assumption to build 10 identical units in order to optimize the construction costs. Table 3 gives the plant cost estimate as percentage of the delivered equipment costs (Peters and Timmerhaus, 1980). Such estimate does not include either hydrogen storage vessel either high-pressure hydrogen compressor. On table 4 the various components (Variable Operating Costs, Operating & Maintainance costs and depreciation) and the overall result expressed in terms of Euro per m^3(STP) of hydrogen produced are listed.

Table 3. *Investment costs estimation*

	10^3 Euro	%
Equipment cost (delivered including PLC)	450	100
Bulk materials (piping, instrumentation, electrical, etc.)	150	33
Equipment and bulk material outside b.l.	200	44
Total direct costs	**800**	**177**
Engineering	50	11[*]
Construction	300	67
Total direct+indirect costs	**590**	**255**
Contractor profit and project contingency	100	22
Total investment Cost	**1250**	**277**

[*] engineering cost have shared on 10 identical units

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Table 4. *Hydrogen production cost*

Case	VOC	O&M	Depreciation rate	Total Euro per m^3(STP)
ATR technology	0.13	0.04	0.36	0.53

4. Conclusions

The feasibility of a hydrogen based distributed power generation has been examined from both technological and economical point of view. The methane catalytic ATR technology was chosen for H_2 production. Results of catalytic activity tests performed on the Engelhard ATR7B catalyst supported on monolith and SiC foam showed that both system are able to assure a stable methane conversion and hydrogen production very close to the equilibrium value even at very high GHSV values. In particular, experimental results showed that ATR7B supported on ceramic foam allows average temperature values considerably lower and a more uniform temperature profile, suggesting that the cellular structure is a very good candidate for the development of an alternative scheme based on an ATR reactor integrated with a membrane inside the catalytic bed for hydrogen separation. From the economical point of view, although the ATR technology results in very compact and simple to be operated units, suitable for small scale distributed production, the manufacturing costs at least for a capacity of $50m^3$/h (STP) is not so high (SRI Consulting, 2003). However, such a result can allow to compare different options and evaluate the competitiveness of small-size hydrogen plants versus larger units.

Acknowledgements

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