

Hydrogen generator, via catalytic partial oxidation of methane for fuel cells

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Abstract

It is well known that the most acknowledged process for generation of hydrogen for fuel cells is based upon the steam reforming of methane or natural gas. A valid alternative could be a process based on partial oxidation of methane, since the process is mildly exothermic and therefore not energy intensive. Consequently, great interest is expected from conversion of methane into syngas, if an autothermal, low energy intensive, compact and reliable process could be developed. This paper covers the activities, performed by the CNR Institute of Transformation and Storage of Energy (CNR-TAE), on theoretical and experimental studies for a compact hydrogen generator, via catalytic selective partial oxidation of methane, integrated with second generation fuel cells (EC-JOU2 contract). In particular, the project focuses the attention on methane partial oxidation via heterogeneous selective catalysts, in order to: demonstrate the basic catalytic selective partial oxidation of methane (CSPOM) technology in a subscale prototype, equivalent to a nominal output of 5 kW_e; develop the CSPOM technology for its application in electric energy production by means of fuel cells; assess, by a balance of plant analysis, and a techno-economic evaluation, the potential benefits of the CSPOM for different categories of fuel cells. © 1998 Elsevier Science S.A.

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1. Introduction

The steam reforming of methane (SRM) is endothermic ($\Delta H_{298} = 206$ kJ/mol) and high H₂O/CH₄ ratios are required in order to limit coke formation at T higher than 1000 K. Moreover, it is a common practice that the process's fuel economy is highly sensitive to appropriate heat fluxes and reactor design (tubular type) and to operational conditions. Efficient heat recovery can be accomplished only on large scale units (>40 000 N m³/h), far from the range of interest for 'on-site' fuel cells. Even if, to fit the needs of the fuel cell technology, medium sized external reforming units (50–200 N m³ H₂/h) have been developed and/or planned for integration with both the first and second generation fuel cells, ameliorations in their heat recovery and efficiency are at the expense of an increased sophistication and therefore a higher per unit cost. In all cases, SRM requires an 'extra fuel' supply (to sustain the endothermicity of the reaction) in addition to stoichiometric requirements ('feed' gas). A valid alternative could be a process based on catalytic partial oxidation of CH₄ (CSPOM), since the process is mildly exothermic ($\Delta H_{298} = -35.6$ kJ/mol) and therefore not energy intensive.

The experimental work [1], carried out by CNR-TAE, in the framework of the JOULE II Program Fuel Cell (funded in part by the Commission of the European Communities), covered the following approaches.

- Design and construction of a sub-scale adiabatic reactor prototype of 5 N m³/h of hydrogen (5 KW_e equivalent) with an optimised geometry in order to combine a set of the most proper catalyst and engineering key characteristics such as: linear (ca. 1 m/s) and spatial velocity (GHSV = 80 000 h⁻¹), diluent to the catalyst ratio (3:1), choice of catalyst particle size (3 × 3 mm), O₂/CH₄ ratio (0.50–0.55), temperature (1073–1173°K), pressure (1–3 bar), etc. The main key features, upon which the prototype design was based, were the following: simple design, easy construction, high compactness, good flexibility, high reliability, low cost, low maintenance, high safety.
- Experimentation of said prototype seeking to establish reaction conditions which would assure long endurance and stability as well as to give a response to feed changes, accidental or provoked events, start-up and shut-down, etc.
- Balance of plant analysis, in order to make an assessment of the requirement for gas clean-up

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and of the basic design of the integrated system ‘fuel processor–fuel cell’.

- Techno-economic evaluation, based upon advantages and proven and/or expected savings, from the introduction of the CSPOM concept in combination with different categories of fuel cells (i.e. solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs), phosphoric acid fuel cells (PAFCs), solid polymer electrolyte fuel cells (SPEFCs)).

2. Experimental

A scheme of the hydrogen generation system (Model CSPOM1/01) is depicted in Fig. 1. It is possible to distinguish two parts: one (closed in the square) works at a high temperature, the second at ambient temperature. The high temperature side include a fixed bed reactor, a heat exchanger (N.1, double-pipe exchanger) and a burner coupled with the second exchanger (N.2).

The low temperature side consist of a mixing reactor, manual and automatic valves, pressure regulators and transducers, flow meters and ancillaries.

The tubes for the high temperature side are in Stainless Steel 310 S, while the latter, for ambient temperature, are in Stainless Steel 316.

During the start-up, nitrogen is sent to the heat exchanger N.1 (internal tube), to the heat exchanger N.2, to the reactor, to the heat exchanger N.1 (external tube) and then to vent.

When the temperature of the catalytic bed is ca. 400–500°C the nitrogen is stopped and air, mixed (in the mixing reactor M) with methane, is sent to the reactor: the mixture air–methane is preheated in the heat exchanger N.1 by the reaction products.

During the shut-down, air and methane are shut off and nitrogen sent as a purge. The alarms circuit foresees an automatic cycle of shut-down for some different events: max. pressure, min. pressure, high temperature, low temperature, gas leakage. The max. temperature is regulated by thermocouples located at 0.25 and 0.50 of the bed length.

There are, also, various connections with a gas chromatograph (Carlo Erba Model 6000): reactants and products at 0.25 and 0.5 of the bed length are analysed by gas-chromatography.

The CSPOM1/01 reactor, capable of producing 5 N m³/h of syngas (H₂ + CO) is a compact tube in Stainless Steel 310 S. The catalyst volume is only 85 cm³, diluted with an inert (alumina, catalyst/alumina ratio = 1:3) to overcome temperature gradients (‘hot spots’), the internal reactor volume is 637 cm³.

On the basis of the procedure identified during the micro-scale tests [2], some preliminary runs have been carried out to check the prototype and to verify the correct procedure methodology.

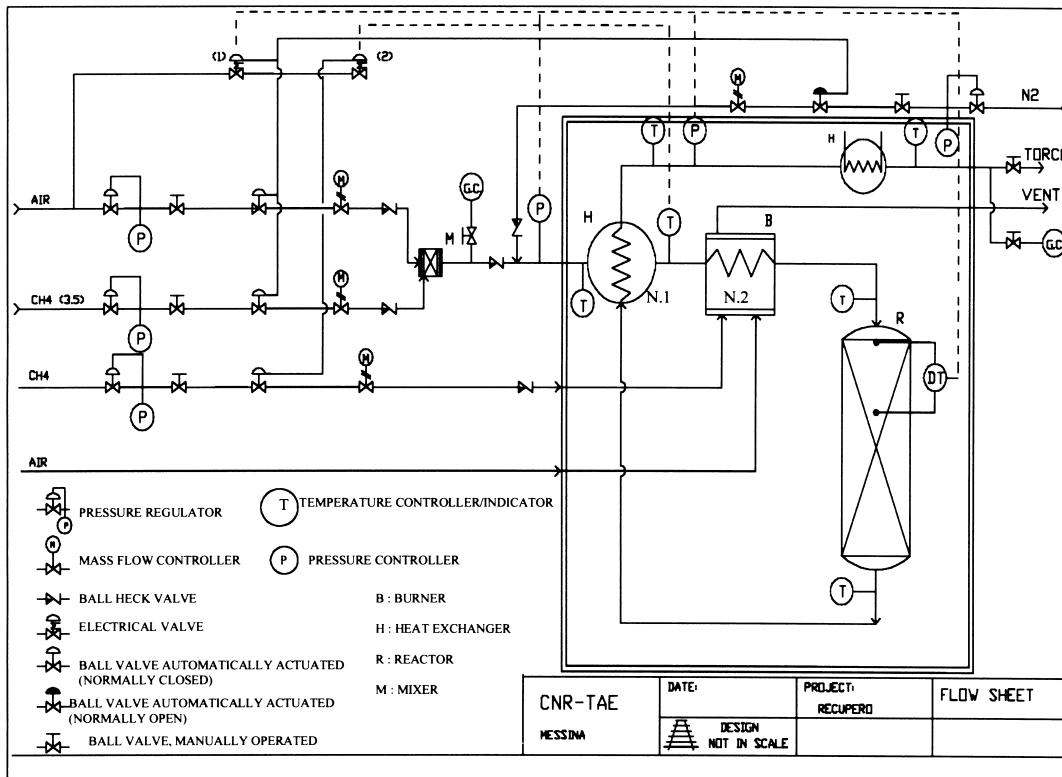


Fig. 1. Flow sheet of the CSPOM1/01 prototype, (5 N m³ H₂/h).

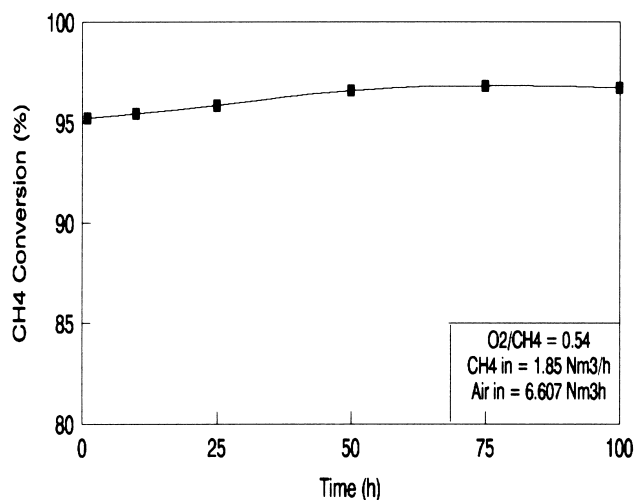


Fig. 2. CH₄ conversion vs. life time. CSPOM1/01 prototype (5 N m³ H₂/h).

The working conditions of the first series of tests are: catalyst CRG-F (British Gas), size 3 × 3 mm (pellets); $P = 1\text{--}4$ bar; $T = 1073\text{--}1173^\circ\text{K}$; $\text{O}_2/\text{CH}_4 = 0.50\text{--}0.55$; $\text{GHSV} = 80\,000\text{ h}^{-1}$.

3. Results and discussion

The tests, in the 5 N m³/h syngas prototype, have shown the proof of the concept; the results confirmed the expectations: methane conversion of 97%, stable during the run time (Fig. 2); oxygen conversion close to 100%; CO and H₂ selectivity of 99% (Figs. 3 and 4); H₂ yield of 95% (Fig. 4), showing a negligible formation of water. A deposition of carbon, during the tests, was closely correlated, in our case ($\text{O}_2/\text{CH}_4 = 0.50\text{--}0.55$) with the procedure of start-up of the different tests. In fact, the results obtained both at lower and higher ratios, have pointed out an amount of carbon more consistent than the theoretical yield. Therefore, there are two possible mechanisms for carbon deposition, the Bou-

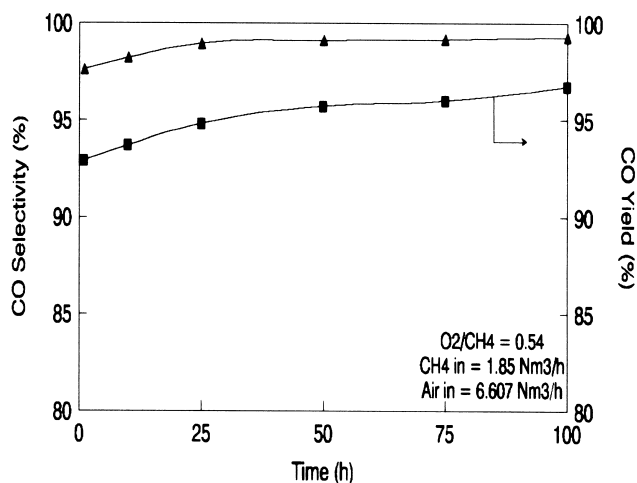


Fig. 3. CO selectivity and yield vs. life time. CSPOM1/01 prototype (5 N m³ H₂/h).

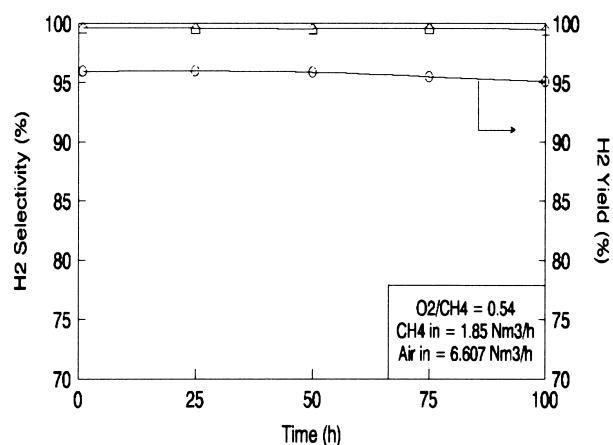


Fig. 4. H₂ selectivity and yield vs. life time. CSPOM1/01 prototype (5 N m³ H₂/h).

douard reaction (Eq. 1) or the catalytic methane reaction of decomposition (Eq. 2).



A non-correct procedure of the start-up (inhomogeneous distribution of the temperatures in the catalytic bed) can favour reaction (1) or (2), depending upon the range of the temperatures in the catalytic bed. The analysis of the temperature in the catalytic bed, by the thermocouples placed inside the reactor, showed, particularly during the start-up step, a non-optimal distribution of the temperatures (some local temperature close 720°C). This problem is emphasised, particularly, when the mixture air–methane is sent to the reactor at a temperature between 400 and 500°C (to avoid some over-heating in the catalytic bed).

A mathematical model has been developed to study the adiabatic temperature profile along the catalytic bed. The modelling approach has been adopted to derive, from the analysis of theoretical results, useful information to design a reactor capable of assuring quasi-isothermal conditions,

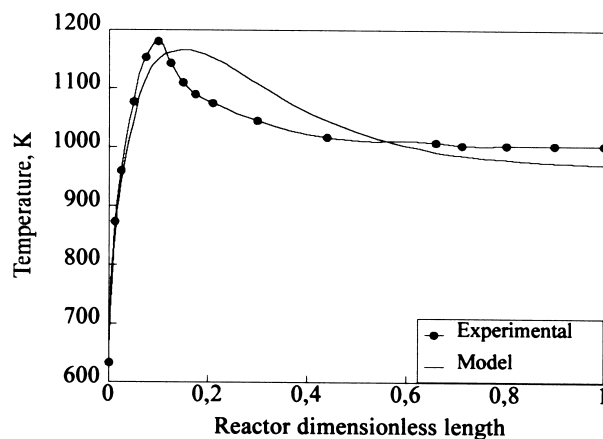
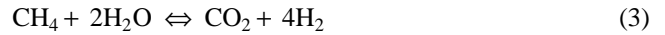


Fig. 5. Comparison between experimental and calculated (model) temperature profiles.

such as to avoid hot spots in the catalytic bed. The model is based on the following main assumptions: (i) reaction controlled by mass transfer; (ii) composition of the reaction mixture at the catalyst surface, in thermodynamic equilibrium with the bulk-flow one; (iii) temperature of the catalyst surface, equal to the main-stream one; (iv) axial profile of temperature, negligible. Besides, to obtain a careful estimation of the longitudinal temperature and composition profiles, various partial methane oxidation reaction models, derived from the literature [3,4], have been considered and analysed. However, the model results, confirmed that the reaction pathway involves initial conversion of some CH₄ to CO₂ and steam, followed by a sequence of steam reforming and water gas shift reactions, to give equilibrium product yields. In Fig. 5 the longitudinal temperature profiles obtained by the model are compared with experimental results: the agreement between the simulation results and the experimental one has been sufficiently high. In fact, the behaviour of the temperature profile calculated by the model is very similar to the experimental one, even if a broad peak of temperature results from the model calculations. Further model improvements will be addressed to eliminate these disagreements.

Besides, the requirements for clean-up of gases has been identified according to the category of fuel cells, as follows. For both SOFCs and MCFCs, which can accept CO, no clean-up is necessary. For PAFCs, a reactor for water gas shift reaction (WGSR) will be necessary. For SPEFCs, besides the WGSR, a catalytic reactor for the total abatement of CO will be further considered in cascade. Other key features concern: (a) hydrogen that is not consumed in the anode has to be utilised in other sections of the integrated system, to maximise thermal efficiency; (b) utilisation of the energy of every stream in the system must, also, be maximised; therefore, a considerable effort goes into the optimum use of heat exchangers, condenser and other energy exchange devices. As regards point (a), in the steam reforming fuel processor the un-reacted hydrogen is fed to the reformer furnace and supplies most, if not all, of the energy requirements for the endothermic steam-hydrocarbon reactions. In systems that do not require energy to process the

fuel (such as autothermal reforming and partial oxidation) other uses must be found for the anode exhaust gas, in order to maximise the efficiency (i.e. the use of a membrane to separate hydrogen in the fuel cell). On the other hand, the perceived potential which makes the CSPOM a pursuable alternative to SRM is implicit when the overall fuel specific consumption, of the two processes are compared. For SRM:



the stoichiometric ('feed') requirement is 0.28 N m³ CH₄/N m³ H₂ (90% conversion of CH₄). Because of its high endothermic character and other inefficiencies, an extra amount of CH₄ fuel is necessary. A survey of published information shows that for typical medium sized plants (1500 N m³ H₂/h), the total 'feed' + 'fuel' requirement is in the order of 0.45 N m³ CH₄/N m³ H₂ (Table 1).

Because of scale's economy, larger units (>40 000 N m³ H₂/h) allow a lower consumption down to 0.41 N m³ CH₄/N m³ H₂. However since H₂ for fuel cells is a commodity not available 'over the counter', a comparison with figures for typical small sized plants (200 or ever 500 N m³ H₂/h) like those marketed for the 50–200 kW PAFC is compulsory. According to specifications given by companies, 'minimum' specific consumption on such plants is in the order of 0.45 N m³ CH₄/N m³ H₂ or 4000 kcal/N m³ H₂ (based on lower heating value (LHV)) which should thus be taken as a reference for the comparison.

Conversely, as the CSPOM is mildly exothermic:



the total net specific consumption is exclusively dictated by stoichiometry (0.33 N m³ CH₄/N m³ H₂), which for a specific CH₄ conversion of 90% gives 0.36 N m³ CH₄/N m³ H₂. Moreover, it is important to stress that this specific consumption is, by definition, insensitive to the size and this allows one to anticipate flexibility, as to the size required for the fuel processor modules, totally lacking in conventional steam reforming. From the above, it is evident that the CSPOM allows a saving with respect to conventional SRM, varying, depending upon the size, from 12 to 20% in the fuel consumption per unit CO and H₂ (KTI, Mannesmann Group, pers. commun.) [5]. The comparison, in terms of productivity, is also in favour of the CSPOM. As typical contact times for total conversion of CH₄ are in the order of 0.04 s, a productivity of 0.3–0.5 mol CH₄ converted/kg catalyst per second is expected, which is at least one order of magnitude higher than that reported for most efficient SRM plants. Therefore, it could be anticipated that CSPOM will demand a reactor size at least one order of magnitude smaller, with inherent savings in investments which preliminary estimates assume to be in the order of 30%. Technical benefits, as above, should be weighted, on the side of investments, in lower amortisation rates with the additional benefits of an easier workability and a more compact assembling bound to the adiabatic vs. the tubular configuration.

Table 1

Performance data per 1000 standard cubic feet (26.8 Nm³) hydrogen based on a typical medium sized plant (1500 N m³ H₂/h), (KTI, Mannesmann Group, pers. commun.)

Case	1	2	3	4	5
Feed and fuel(MBTU)	430	434	448	430	589
Specific consumption (Nm ³ CH ₄ /Nm ³ H ₂)	0.45	0.455	0.47	0.45	0.62

Case 1, standard hydrogen plant, reforming without air preheat using only a high temperature shift reactor; case 2, case 1 including a low temperature shift reactor; case 3, case 1 including gas turbine exhaust as combustion air (enthalpy of air included); case 4, case 1 generating electricity with the available steam; case 5, case 4 with auxiliary firing in the convection section. MBTU, mega British thermal unit.

Table 2

Main advantages and disadvantages of the hydrogen generator via methane partial oxidation system in different fuel cells

Fuel cell	Advantages	Disadvantages
Solid polymer electrolyte	Very fast response to the load variations Compactness Reliability Low cost	Need of the WGSR and CO Selective oxidation subsystem Need to optimise the use of exhaust hydrogen of the fuel cell Need to optimise the thermal balance
Phosphoric acid	Very fast response to the load variations Compactness Reliability Low cost	Need of the WGSR subsystem Need to optimise the exhaust hydrogen of the fuel cell Need to optimise the thermal balance
Molten carbonate and solid oxide	Direct use of the gas outgoing from CSPOM Very fast response to the load variations Compactness Reliability Low cost	Need to optimise the thermal balance

Besides, because of its lower heat enthalpy, promptness to start-up and shut-down in CSPOM is expected to be higher and to better follow the changes in the load of the fuel cell subsystem. It should be noted that the theoretical debit for using 50% syngas rather than 100% (due to the use of air) results in a loss of only 15 mV in open circuit potential, a trivial disadvantage. Furthermore, as the adiabatic characteristics of a CSPOM reactor would demand less stringent engineering geometry and regulations, a wide ‘degree of freedom’ in the modularity of use is

expected, making it possible to respond to site-specific needs.

Altogether, volume, unit costs, reliability, commitment to user’s requirements add in anticipating the high competitiveness of a CSPOM based fuel economy with respect to most traditional means of a syngas and/or H₂ generation. As, with the addition of some proper gas clean-up processes, the quality of gas can be adjusted to fit the requirements of even the most demanding fuel cells (PAFCs, SPEFCs), the ‘as claimed’ CSPOM concept should be considered of a more

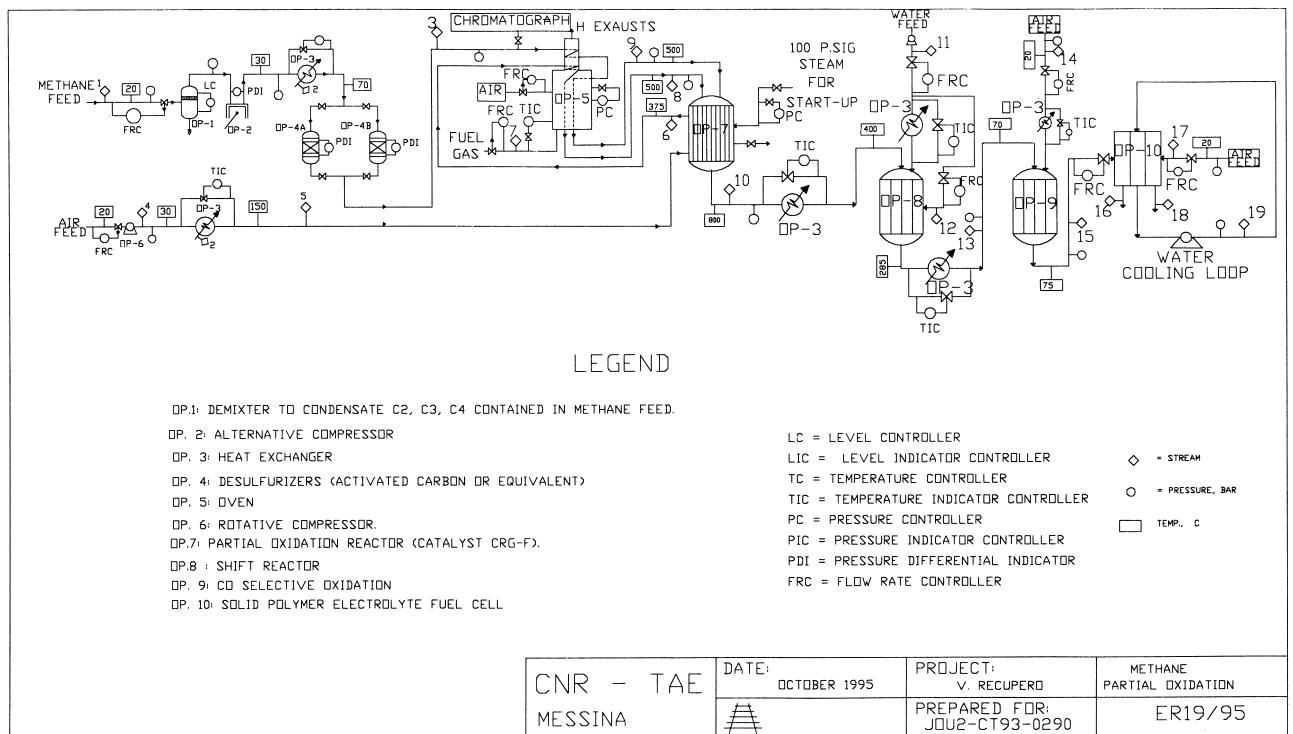


Fig. 6. Detailed scheme of the integrated system hydrogen generator–solid polymer electrolyte fuel cell.

Table 3

Methane partial oxidation system: mass balance, related to Fig. 6

	1	4	7	10	11	12	13	14	15	16	17
CH ₄ (kmol/h)	0.0826		0.0023	0.0025			0.0025		0.0025	0.0025	
Air (kmol/h)		0.2167						0.135			0.8923 ^a
H ₂ O (kmol/h)				0.0208	0.1395	0.0620	0.0845		0.0845	0.0572	
H ₂ (kmol/h)				0.1393			0.2149		0.2149 ^b	0.0645	
CO (kmol/h)				0.0793			0.0037				
CO ₂ (kmol/h)				0.0008			0.0764		0.0801	0.0801	
N ₂ (kmol/h)				0.1708			0.1708		0.2774	0.2774	
Temperature (°C)	20	30	20	800	20	20	70	70	70	72	20
Pressure (bar)		4						3.5	2.5	2.5	3

^aAir utilisation: 50%.^bH₂ utilisation: 70%.

general validity and strategical importance. Table 2 summarises the main advantages (and disadvantages) of the methane partial oxidation system applied in various fuel cell generations; while Fig. 6 shows the detailed scheme proposed for the integrated system hydrogen generator–solid polymer electrolyte fuel cell; Tables 3 and 4 show the mass and the heat balance of this proposed system, respectively.

4. Conclusions

In the framework of the JOULE II Program, CNR-TAE developed a hydrogen generator for fuel cells based on the catalytic partial oxidation of methane. In this respect, the following main conclusions can be drawn:

- a commercial Ni/Al₂O₃ catalyst (CRG-F) has been selected for catalytic tests;
- the 5 N m³/h of syngas prototype has been designed and assembled;

- the working runs have been successfully carried out;
- the main results are: methane conversion close to 97%, oxygen conversion close to 100%, selectivity to carbon monoxide close to 99%, selectivity to hydrogen close to 99%;
- distribution of the temperature sufficiently uniform along the catalytic bed has been obtained.

Furthermore, an analysis, to provide background for applications of the CSPOM concept to fuel cell technology, has been carried out. In particular, different hydrogen generators have been analysed to identify the best system to be integrated with the different generations of fuel cells; an economic comparison has, also, been accomplished between the methane partial oxidation system and methane steam reforming. The basic schemes and the detailed configuration of the hydrogen generator fuel cell (SPEFC, PAFC, MCFC, SOFC) have been identified. The analysis gave an indicative, although firm, estimate of savings in investments and utility consumption per unit energy pro-

Table 4

Methane partial oxidation system: heat balance, related to Fig. 6

	Heat (Kcal/h)
Q1 (fuel preheating from 30 to 70°C)	26.40
Q2 (air preheating from 30 to 120°C)	141.40
Q3 (fuel heating from 70 to 500°C) ^a	406.35
Q4 (heat released from partial oxidation reaction)	680.55
Q5 (air heating from 120 to 455°C) ^a	510.60
Q5' (air heating from 455 to 500°C) ^a	70.70
Q6 (fuel cooling from 800 to 400°C)	1202.70
Q7 (water heating from 20 to 400°C)	1060.20
Q7' (water heating from 20 to 215°C) ^a	750.70
Q8 (heat released from the WGS, HT)	404.20
Q8' (fuel cooling from 505 to 215°C)	1089.30
Q9 (heat released from the WGS, LT)	285.10
Q10 (fuel cooling from 285 to 70°C)	900.15
Q11 (air heating from 20 to 70°C)	49.00
Q total (Q1 + Q2 + Q3 + Q5 + Q5' + Q7 + Q7' + Q10) – (Q4 + Q6 + Q8 + Q8' + Q9 + Q10)	–1546.65

^aHeat exchanger effectiveness (hypothesis) = 80%.

duced by such integrated systems, confirming the technical and economical advantages of the catalytic partial oxidation system vs. the classic steam reforming. Work in progress has been addressed to analyse some other main aspects: particularly, the use of natural gas, instead of methane (stability of the catalyst to sulphur); the regeneration of the catalyst, material compatibility, etc.

Acknowledgements

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