DOUBLE-EXCHANGE NATURAL GAS REFORMER COUPLED WITH A PEM FUEL CELL

Christian Hamon\textsuperscript{a}, Gwénola Le Moël\textsuperscript{b}, Paul Gateau\textsuperscript{b}, Lucile Voiron\textsuperscript{c}, Valéry Chaudron\textsuperscript{c}, Grégory Bertrand\textsuperscript{d}, David Le Noc\textsuperscript{d}

\textsuperscript{a}IRMA – 9, rue Galilée – B. P. 64 – F-56274 Ploemeur Cedex – France – irma@wanadoo.fr
\textsuperscript{b}LOIRE 2IS – 21, rue de la Poterie – 44640 St-Jean de Boiseau – gateau.paul@wanadoo.fr
\textsuperscript{c}HELION – Domaine du Petit Arbois – Bâtiment Beltram – BP 71 – 13545 Aix en Provence Cedex 04 – lucile.voiron@helion-fuelcells.com
\textsuperscript{d}GAZ DE France – 361, avenue du Président Wilson – BP 33 – 93211 Saint-Denis La Plaine Cedex – gregory.bertrand@gazdefrance.com

ABSTRACT:

The equipment described hereafter has been developed within the REFoPEM program from the PACO network and co-funded by the “Agence de l’Environnement et de la Maîtrise de l’Énergie” (ADEME) and GAZ DE FRANCE. The aim of this program was the development, the construction and validation of a reformer / PEM fuel cell prototype, working with natural gas, for residential cogeneration applications. This project is coordinated by GAZ DE FRANCE.

HELION as a fuel cell maker was in charge of the fuel cell module development and construction, its connection to the reformer and the prototype overall integration. The “Institut Régional des Matériaux Avancés” (IRMA) was responsible for natural gas reformer development and construction, and then with HELION, for its connection to the fuel cell.

The reformer/fuel cell prototype must supply an electrical power of about 1 kW.

This paper describes a natural gas double-exchange reformer coupled with a PEM fuel cell.

KEYWORDS : Catalytic reforming of natural gas, Steam reforming coupled with auto thermal reforming, Water gas Shift, Preferential oxidation , PEM fuel cell, residential cogeneration prototype, load following.

1 – INTRODUCTION

The REFoPEM project began in December 2002 and will be completed in September 2006. The main goal was to demonstrate the feasibility of coupling a SR/ATR reformer with a PEMFC keeping residential cogeneration application in mind.

The program is divided into the following three main parts:

1) Developing a low capacity new natural gas reformer (1,5 Nm\textsuperscript{3} H\textsubscript{2} per hour) based on a steam reformer (SR) coupled with an autothermal one (ATR).
2) Performing a 1 kWel PEMFC module, and developing the interfaces to be integrated to the reformer.
3) Testing the reformer / PEM fuel cell prototype and carrying out a technical economical study.

Last point’s results are not mentioned in this paper due to his writing having occurred ahead of the testing of the reformer/fuel cell prototype. The results of integration will be exposed at the time of the conference.
2 – NATURAL GAS REFORMER

2.1 Reforming methods overview

Producing hydrogen from natural gas is currently practiced in the chemical industry (1). The most exploited industrially is the steam reforming (SR). It is generally followed by an oxygen or air working reforming reactor called secondary reformer (2)(3). Alternative ways are proposed such as the autothermal reforming (ATR) (4) or partial oxidation (POX) (5).

For this study, hydrogen is produced by a SR-ATR coupling which has already been reported in many publications (6)(7).

The natural gas reformer for hydrogen production is a catalytic system under pressure (4 bara). As catalysts are sensitive to sulphur, natural gas first goes through a desulphuration column. The sulphur content is reduced to less than 1 ppm by adsorption on a microporous solid.

SR and ATR catalysts are precious metals based catalysts under monolith form (8): metallic for the SR in order to improve thermal exchanges and ceramic for the ATR. Shift is a transition metals oxides based catalyst in the shape of extrudates, and PROX a precious metals based catalyst in the shape of pellets.

2.2 Experimentation

The development of the whole reformer starts with the tests on the elementary catalytic steps in order to define the operating conditions necessary to reach high efficiency. The experiments have been carried out in fixed bed reactors surrounded with ceramic fiber heaters, under a simulated atmosphere. The five stages, SR, ATR, Shift, PROX and post oxidation have been studied.

The most interesting results of our experiments are reported hereafter:

- **SR-ATR Coupling:**

  A prototype unit has been built in order to prove the feasibility of this reactor-exchanger concept. The 1” diameter reactor is loaded at the inlet with a catalyst of steam-reforming followed by an autothermal one. Air is introduced between the two catalysts. The reaction on the autothermal catalyst is exothermic. The hot gases leaving the ATR (~700°C) flow around the steam reforming reactor providing the required energy for the endothermic reaction. Reagents pre-heating and water vaporization were ensured by electric heaters, because catalytic oxidation of fuel cell anode off gas (H₂ not consumed and CH₄ not converted) was not integrated in this part of the experimentation.

  In Fig.1 temperatures evolution according to O₂/C ratio is shown at several places where the reactions occur:

![Fig.1. Temperature evolution according O₂/C ratio](image-url)
The system great reactivity to O₂/C ratio variations has to be mentioned. It contributes to an added asset: the flexibility on the process. In addition, these results match those expected in term of effectiveness; in the following conditions: H₂O/C = 3 and O₂/C = 0.45, 95% of natural gas is converted and the efficiency of the reformer is evaluated to 76%.

• **Shift:**

The water gas shift reaction has to reduce the CO content of the reformate to 0.5 % or less (9). Shift reaction (CO + H₂O ↔ CO₂ + H₂) is governed by thermodynamics and CO content is function of inlet gas composition and temperature. Obtained CO concentrations (% dry gas) are compared in fig.2 to CO contents at the equilibrium for two GHSV (2000 and 4000 h⁻¹ on dry gas) and two inlet gas compositions (CO: 6 and 8 % on dry gas; 50% (dry) H₂; 25 % water vol.):  

![Fig.2. Shift catalyst performance](image)

Some CO contents are below equilibrium. That is naturally impossible. This is due to an uncertainty on the real temperature measurement at the reactor outlet. One can however conclude that balance is reached for a rather standard GHSV (2000 h⁻¹) and for a catalyst outlet temperature between 230°C and 240°C, that is to say about 210 °C at the inlet. It is appropriate to consider that CO contents at the shift reactor outlet will be close to 0.5 %, easing the running of the PROX. Moreover only one stage for the Shift reaction is needed. That is interesting for simplifying the process.

• **CO preferential oxidation (PROX)**

The CO concentration (% dry gas) at the shift reactor outlet is between 0.5 and 1%. By means of a controlled air addition, CO is oxidized into CO₂ in the preferential oxidation reactor to no more than 10 ppm. This oxidation has to be the most selective as possible towards carbon monoxide in order to limit the hydrogen oxidation:

\[
\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \\
\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}
\]

This reaction is hard to manage as described in many publications (10). Trials are carried out with a noble metals based catalyst in the shape of pellets. The steam concentration at the shift reactor outlet is about 22 % (vol.). Several experiments have shown that it was essential to lower the steam concentration by condensation and to operate at very low, even at room temperature. Indeed due to the exothermicity of these reactions, catalyst temperature rises, and carbon monoxide selectivity decreases. That leads to the conception of a nearly isothermal reactor for the prototype unit.
Few results will be indicated in Fig.3 according to inlet catalyst temperature and O₂/CO ratio.

![Fig.3. PROX catalyst performance](image)

- Prototype unit

The simplified process diagram is shown in fig.4 and the prototype unit in fig.5.

![Fig.4 : Process diagram](image)

![Fig.5 : Prototype Unit](image)

The process consists of a steam reforming reactor associated to an air autothermal reforming one. Both are integrated into a double exchange reactor. Steam and natural gas first go through the SR catalyst where the energy needed for this endothermic reaction is supplied by a double exchange, respectively with the ATR outlet gas and the post oxidation fuel cell anode off gas. The SR stage maximizes energy recovery, avoiding at the same time coke formation inherent to a strong pre-heating when high efficiencies have to be performed by an ATR alone. The compromise between the respective contributions of SR and ATR in the natural gas transformation called for an investigation in view to achieve the optimum system performance.
Outlet gas is cooled by a multi-exchanger necessary for steam, natural gas and air pre-heating. Then, it goes through a shift catalyst at about 250 °C in one single stage. At that time, after condensation, it follows its course through a CO preferential oxidation reactor (PROX) at a temperature about 70 °C. The CO concentration (% dry gas) at the Shift reactor outlet is below 1 %, which minimizes PROX exothermicity. Due to condensation, the PROX catalyst can operate at low temperatures, which contributes to achieve easily the 10 ppm of carbon monoxide’s target.

The reformer supplies the fuel cell with a gas containing carbon dioxide, nitrogen and about 50 % H₂. Residual methane is less than 3 % vol.

Hydrogen supplied by the reformer is not pure. Due to both the dilution effect and the flow through operation, it remains some hydrogen at the fuel cell stack output.

Fig. 6: Double exchange natural gas reformer

The energy of post oxidation hot gases is used for the water vaporization and the reagents (GN and air) pre-heating. In order to control the CO content at the outlet of the shift and PROX reactors, a circulation of coolant is integrated to achieve a nearly isotherm running.

This unit was brought into service gradually. Temperature evolution is measured at various process stages: SR, ATR, Shift, PROX, and post-oxidation for which reaction, the fuel cell anode off gas is simulated by a H2/N2/CO2 mixture.

The reformer is fed with natural gas. The operating conditions are as follows: H₂O/C = 3; O₂/C = 0,4; simulated fuel cell anode off gas = 50 % of the hydrogen produced.

For an inlet shift temperature of 240°C, we obtain at the outlet the following concentrations: 52.2 % H₂; 17 % CO₂; 29.4 % N₂; 1% CH₄ and 0.4 % CO.

Test performed on the final prototype has permitted to validate the expected specifications:
- Production of a high content H₂ effluent (H₂ content about 55 % - Flow rate: 1,5 Nm³/h hydrogen)
- CO concentration: lower than 10 ppm
- Electrical auxiliaries demand: 120 Watts
- Efficiency (outlet hydrogen LHV / inlet NG LHV): higher than 75%.

The 50 % H₂ content effluent is supplied to the fuel cell stack through a modulating valve driven by the fuel cell automation system. This valve follows electrical demand and brings about the modification of natural gas, air and water flow rates thanks to reformer automation system which controls all the operating parameters such as H₂O/C (SR), O₂/C (ATR) and O₂/CO (PROX) and maintains shift and PROX reactors temperature. It communicates also with the fuel cell automation system for starting and transitory stages management. A second automation unit is dedicated to security (lack of reagents feeding for example).

3 – DESCRIPTION OF THE FUEL CELL MODULE OPERATION

The stack is the place where the electrochemical reaction occurs to transform oxygen from the air and hydrogen from the reformat blend to produce DC electricity and heat. The catalyst on the hydrogen side is a PT-Ru alloy in order to handle the 10 ppm CO present in the reformat. The 40 cells stack has a 100 cm² active surface area. The stack operates at 55% electrochemical efficiency. The other part is transformed into heat to be recovered by an outside boiler.
Air compressor and modulating valve bring respectively the proper air and hydrogen flows to the stack inlets. The primary cooling loop controls the stack temperature thanks to a heat exchanger with the secondary loop. The secondary cogeneration loop recuperates heat produced by both the stack and the reformer to be recovered by an outside boiler. The FC module (see fig. 7) has lots of instrumentation device for complete characterisation that would not be required for an industrial unit.

Fig.7. Fuel cell module

4 – DESCRIPTION OF THE REFORMER- PEM FUEL CELL MODULE

Reformer / PEM fuel cell coupling is an attractive equipment for stationary applications. During last years, several systems of this type were developed and then evaluated in real conditions (11) (12).

The overall prototype (see fig.8) is supplied with natural gas to produce DC electricity and heat.

Fig.8. Reformer / PEM fuel cell diagram

During start up the auxiliaries are fed by the grid. After reformer module warmed up, purified reformat is sent to the stack thanks to the modulating valve at the FC module inlet. The stack starts producing current to feed the auxiliaries. Then when stack operational temperature is reached the load contactor is closed and loads profiles can be performed on the prototype. The prototype follows electrical load demand. The main idea was to evaluate the response time of such process, SR/ATR reformer coupled with the PEM FC stack and to define possible product integrating this process to meet customer needs for residential cogeneration applications.
Two main load following logics were evaluated. The idea is to adjust both reformat and air flows as a function of the power demand or as a function of the anticipated power demand.

The load (that simulates the house) is controlled by the prototype user through a friendly GUI (Graphical User Interface) and the evaluation of the process response time as a function of different parameters such as hydrogen and oxygen stoichiometries and control logics was investigated.

Different products architectures were defined integrating this process to answer different customer needs.

First when the prototype is connected to the grid, its goal is to supply the average electrical or thermal power to meet house needs. The electrical average power of a house is below 1kWel. Peak power above this average power is supplied by the grid.

Then when the prototype is not connected to the grid, during a network breakdown, the system’s goal is to supply power to maintain the minimal house apparatus. The system behaves like a UPS for a part of the house apparatus previously chosen, while the others are disconnected from power.

Finally when the prototype is not connected to the grid in a remote area the prototype includes a battery bank for start up, transient and peak power.

CONCLUSION

The catalytic reformer coupled with the PEM fuel cell described in this paper is the first prototype which has been developed and built in France.

Elementary stages experiments allowed the design of a catalytic reformer which delivered the reliable production of a gas mixture perfectly suitable for a PEM stack.

Moreover, automation systems and safety procedures ensured the following of loads profiles and electrical power demands of the process associated auxiliaries (pressure, flow, temperature control).

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