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High temperature hybrid steam-reforming for hydrogen generation without catalyst

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Abstract

This study is devoted to the experimental characterization of a laboratory-scale hybrid steam-reformer for H_2/O_2 fuel cell applications. The thermal, high temperature process used enables the conversion of a wide range of fuels into a hydrogen-rich gas without catalyst. Last January, this work resulted in the creation of a French start-up named "N-GHY S.A., Fuel Processors for Fuel Cells."
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1. Introduction

The different scientific and industrial actors come to an agreement to think that fuel cell systems should offer many advantages in comparison with other traditional mature ways of energy production. The large-scale utilization of these systems would result in significant energy savings at the planetary scale. Through the raise in efficiency, and the associated diminution of primary energy consumed, fuel cell technology could contribute to lower the atmospheric pollution in urban areas in terms of smokes, poison gases like nitric oxides, exhausts of unburned hydrocarbons and volatile organic compounds, and could attenuate the climate change owing to a reduction of greenhouse gases (especially carbon dioxide) emissions. It could also limit the energetic dependency of some countries, thanks to the utilization of local resources that are not or little exploitable at present.

Given the importance of the market and the adoption of more and more stringent standards and legislation on automobile exhausts, road transport field has become the subject of the most intense international competition in fuel cell technology, between worldwide automobile manufacturers. The latter have concluded that PEMFCs have the best potential to replace the internal combustion engine for propulsion power. Each manufacturer has been evaluating this technology, either in laboratory, or through a more and more common practice of vehicle tests [1]. In order to commercialize H_2/O_2 fuel cell powered vehicles, manufacturers have to face and solve crucial problems referring to the management of the electricity produced onboard by the fuel cell on the one hand, and to the oxygen and hydrogen feeds on the other hand. Concerning the hydrogen feed in particular, the main difficulty lies in the H_2 storage devices. Indeed, it turns out that: H_2 storage is very bulky in gaseous form at 250 or 350 bars, the extremely low liquefaction temperature of H_2 (20 K) makes its storage very delicate in cryogenic liquid phase, and H_2 storage on hydrides leads to heavy (metallic hydrides) or costly (chemical hydrides) apparatus, moreover the high temperatures needed for releasing hydrogen result in slow start-up and make the thermal management system complex. Though H_2 production, storage and distribution are industrially well known and commercially viable technologies, the infrastructure and regulations necessary for its utilization as a fuel for road transport are still missing and many questions are in suspense concerning the realization and the global energetic cost of this infrastructure [2]. As a matter of fact, direct utilization of H_2 by consumers is impossible at present. Thus, to enable the use of H_2/O_2 fuel cell systems in road transport, it is imperative to find a solution to the fuel storage issue.

The first possibility consists in the use of a liquid fuel, directly or indirectly, in the fuel cell. In this way, many

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efforts are being done for the development of fuel cells using methanol as direct or indirect fuel [3]. Nevertheless, as for the hydrogen one, methanol distribution infrastructure is not available and assessments of the cost of its implementation lead to controversies between methanol industrial supporters and automobile manufacturers [4–7]. An other possibility for the solution of the H_2 storage issue resides in the exploitation of the ''indirect'' way. This way invokes a reformer that produces locally, onboard the vehicle, a hydrogen-rich gas, suitable for a H_2/O_2 fuel cell, from hydrocarbons like methanol, gasoline or diesel fuel.
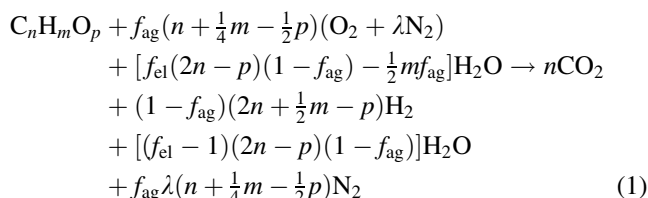
2. Hydrogen production by catalytic processes

There are three ways for the production of H_2-rich gas onboard the vehicle: steam-reforming (SR), partial oxidation (POX) and autothermal-reforming (ATR). SR is the principal route for H_2 production in the industry. This process is based on the reaction of the fuel with steam. This reaction is traditionally achieved over a catalyst and products are H_2 and CO. It is strongly endothermic and its realization requires external inputs of heat, which make the generation system complex and large. In compensation, the molar fraction of the exiting H_2 is high. Methanol SR is carried out at a temperature near 200 °C [8,9], whereas gasoline SR requires temperatures above 800 °C. POX is an incomplete oxidation of the fuel by oxygen. H_2 and CO are also the products of this exothermic reaction, accomplished catalytically or not. No external thermal supply is needed for the POX reaction, but the H_2 molar fraction obtained is lower than the one achieved by the SR process. Gasoline POX is carried out around 1200 °C without catalyst [10,11] and around 800 °C over a catalyst [10–13]. ATR is a combination of the oxidation and steam-reforming processes.

The use of catalysts in reformers, combined with the introduction of microtechnologies, results in low temperature operation modes and in acceptable residence times and volumetric powers. Nevertheless, several significant drawbacks are also associated with the utilization of catalysts. On the one hand, some elements, occurring naturally as hydrocarbon compounds, like sulfur, are recognized as poisons for traditional nickel-based reforming catalysts [14]: this implies an advanced desulfurization of fuels prior to their introduction into the catalytic reformer. On the other hand, steam-reforming on nickel-based catalysts involves a risk of carbon formation, which can lead to the deactivation of the catalysts, or even their destruction, but also and above all cannot be tolerated by the fuel cell [14–17]. Lastly, catalyst selectivity is so acute that each catalyst only enables the reforming of a single molecule or of a range of specific molecules [18]. These drawbacks appear as serious obstacles for the development of a multi-fuel reforming device, capable of converting several fuels or mixtures of different fuels into a hydrogen-rich gas suitable for a fuel cell.

3. Hydrogen production by hybrid non-catalytic steam-reforming at high temperature

An alternative to the use of catalysts is to carry out the reforming operation at higher temperature, according to the Hybrid Steam-Reforming (HSR) reaction. This reaction combines the fuel ($C_nH_mO_p$) with air and steam. Its equation can be written as:

$$
\begin{aligned}
C_nH_mO_p &+ f_{ag}(n + \tfrac{1}{4}m - \tfrac{1}{2}p)(O_2 + \lambda N_2) \\
&+ [f_{el}(2n - p)(1 - f_{ag}) - \tfrac{1}{2}mf_{ag}]H_2O \rightarrow nCO_2 \\
&+ (1 - f_{ag})(2n + \tfrac{1}{2}m - p)H_2 \\
&+ [(f_{el} - 1)(2n - p)(1 - f_{ag})]H_2O \\
&+ f_{ag}\lambda(n + \tfrac{1}{4}m - \tfrac{1}{2}p)N_2
\end{aligned} \tag{1}
$$

where λ is the air molar ratio N_2/O_2. f_{ag} and f_{el} represent the global air factor and the local water factor of the process, respectively; they have been already defined in previous work [19]. This thermal process carried out at high temperature eliminates one of the disadvantages of catalytic processes by enabling the conversion into a hydrogen-rich gas of a wide range of fuels, including ester vegetable oils and even directly vegetable oils. Chemical kinetic calculations on the HSR reaction [20,21] allowed the determination of the operating conditions of a non-catalytic high temperature HSR fed with pure propane: it turns out that a residence time of 1 s enables a H_2 productivity very close to the one given by thermodynamic equilibrium calculations, with only small losses of H_2 productivity, due to the formation and persistence of very small quantities of methane (CH_4), non-methanic hydrocarbons (NMHC) and polycyclic aromatic hydrocarbons (PAH). Those chemical kinetic calculations were used for the conception and realization of a first laboratory-scale HSR of pure propane.

4. Experimental

This laboratory-scale reactor has been designed to operate with or without reactants preheating and up to an absolute pressure of 7 atm. A test bench was also designed and constructed. Its function is to control the environment of the reactor (temperatures, pressures, flows). The nominal operating power of the laboratory-scale HSR with reactants preheating is 7.00 kW (HHV C_3H_8). In the case of a connection with a PEMFC, the electric power aimed at is 3.25 kW$_e$. For the first tests, the HSR reactor operates at atmospheric pressure. Propane and air are introduced at ambient temperature. Water can be injected either in the form of liquid or in the form of steam. In order to reach the high temperatures that favor the steam-reforming reaction, elevated global air factors (f_{ag}) are chosen.

The HSR reactor is composed of two principal zones: the combustion zone and the steam-reforming zone. In the

combustion zone, the fraction f_{ag} of the fuel is burnt in the air. To reduce the formation of nitric oxides, a small proportion of water is also injected and the combustion is carried out in fuel-rich conditions (i.e. the local air factor f_{al} is inferior to 1). The rapidity of the combustion reaction results in a small residence time and hence in a small volume of reaction. During this combustion reaction, taking place at high temperature, free radicals (H, O, OH) are generated. To ensure an intimate mixture between reactants, the design took care of establishing turbulent flows: for this purpose, high speeds of injection and air swirlers are implemented. The heat released by the exothermic combustion reaction of the fraction f_{ag} of the fuel is turned to good account to achieve the endothermic steam-reforming reaction in the steam-reforming zone, where the complementary fraction of the fuel $(1 - f_{ag})$ is introduced with steam. The radicals generated in the combustion zone have an essential role in the decomposition of the molecules and in the initiation of the steam-reforming reaction. The endothermic SR reaction takes place while temperature decreases. Its chemical kinetics is slower than the combustion reaction one. Thus, the SR zone is characterized by a larger volume. To proceed the steam-reforming reaction completely, it is designed to be close to a plug-flow reactor.

5. Results and discussions

A first series of tests was dedicated to the combustion zone: cold ignition and stability diagrams were established for various burner heads, equipped with different propane injectors (provided with six radial orifices or one axial orifice) and different air swirlers (characterized by angles of 15, 30, 45 and 60°). These diagrams show the ignition and stability areas in accordance with the fuel–air ratio of the combusted C_3H_8/air mixture on the one hand, and of the load (total mass flow of C_3H_8 and air) on the other hand. The swirl function is to provide a kinetic momentum to the air flow.

Large swirl angles provoke important gas recirculations which improve the C_3H_8/air mixture, even at low load. The swirler shortens the flame. The axial fuel injection leads to the formation of a stretched flame, whose form is close to a jet. In the contrary, the radial injection shapes a shorter, thicker flame. Globally, the injection hardware constituted by the six orifices C_3H_8 injector and the 30° air swirler presents the widest ignition and stability areas [22].

Another series of tests characterized the thermal operation of the complete reactor. At atmospheric pressure, several tests were accomplished up to a thermal power of 10.8 kW$_{th}$, which represents 150% of the nominal operating power of the reactor. Thus, at an absolute pressure of 3 atm, it will be possible to carry out tests at power levels raising up to 30 kW$_{th}$ or 400% of the nominal operating power. Wall temperatures, measured at different places inside the reactor (both in the combustion zone and in the steam-reforming zone), are consistent with temperatures evaluated from radiato-convective calculations done during the design phase. These wall temperatures are low (<540 °C), thus the operation of the HSR reactor with reactants preheating can be studied safely. Fig. 1 shows the steady state evolution of the gas temperature along the reactor for different operating conditions (the abscissa 0 corresponds to the beginning of the SR zone). This temperature is under-estimated because its measure is realized by a bare thermocouple laid open to the radiation of the cold walls of the reactor. At 64.5 cm from the beginning of the steam-reforming zone, the measured temperature fit in with the temperature obtained by chemical equilibrium calculations when taking thermal losses into account.

Other tests made possible the characterization of the transient states from a chemical point of view. Starting from a cold ignition of the C_3H_8/air mixture, the evolution of the molar composition of the generated gas was determined as a function of time for different operating conditions. In the following configuration: $f_{ag} = 0.37, f_{al} = 0.717, f_{el} = 1.195$,
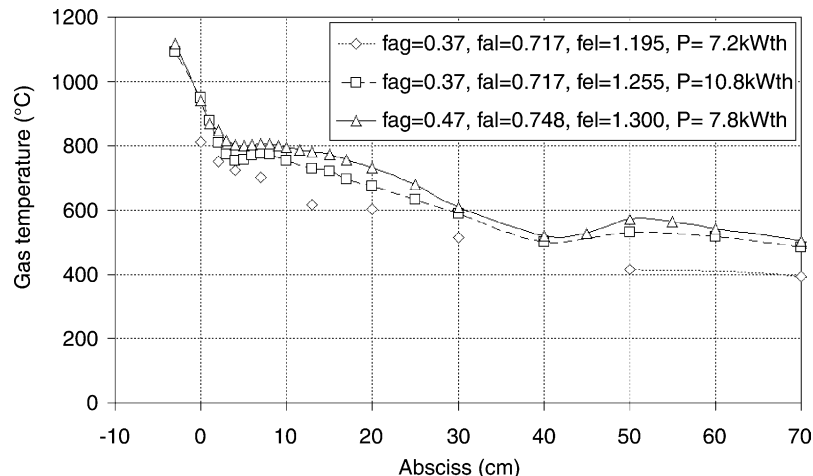

Fig. 1. Steady state evolution of the gas temperature along the HSR reactor for different operating conditions.
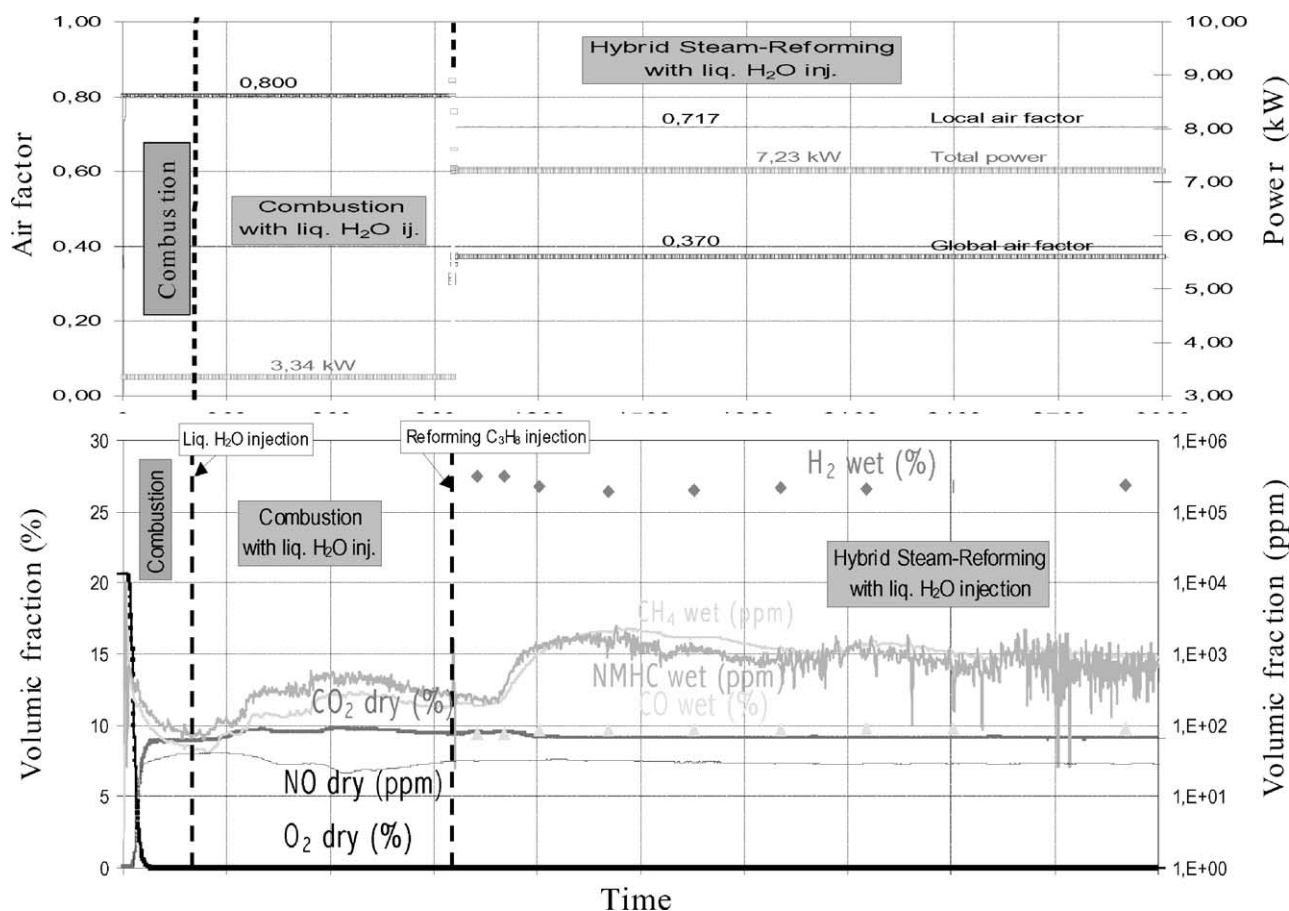
Fig. 2. HSR with liquid water injection: chemical characterization during transient phase (reactants non-preheated, $f_{ag} = 0.37$, $f_{al} = 0.717$, $f_{el} = 1.195$, power = 7.2 kW$_{th}$).

power = 7.2 kW$_{th}$ (HHV C$_3$H$_8$), measures are carried out at the abscissa of 64.5 cm; the following observations can be done (Fig. 2). When the C$_3$H$_8$/air mixture is ignited, a peak of unburnt hydrocarbons (UHC) can be seen (CH$_4$: 0.16%, NMHC: 1.07%), then these UHC become stable around 80 ppmv for CH$_4$ and 110 ppmv for the NMHC (hydrocarbons formation was foreseeable since combustion is realized at a fuel–air ratio of 1.4). During the combustion phase carried out with liquid water injection, the quantity of UHC increases and becomes stable around 180 ppmv for CH$_4$ and 260 ppmv for NMHC. Next, as soon as the complementary fraction of propane is introduced at the beginning of the steam-reforming zone, the HSR phase takes place: H$_2$ and CO are produced and after a few moments their molar fractions reach stable levels close to their equilibrium values.

We have also studied the influence of the global air factor (f_{ag}) and local water factor (f_{el}) on the H$_2$ productivity and on the quality of the generated reformate (persistence of hydrocarbons). For confidential reasons, the results of these tests cannot be presented in this paper. Complementary tests were also realized in order to optimize the start-up of the reactor. It was shown that starting from a cold ignition

hydrogen can be produced after less than 4 min in the partial oxidation mode. We are confident that this start-up time can be further reduced by an adapted automated control system.

6. Conclusions

The first experimental results presented here show that our reforming test bench is an operational, flexible device. Its operation appears satisfying at atmospheric pressure: wall temperatures are acceptable, quick starts are realized and H$_2$ production takes place after only a few minutes. Operations at more elevated powers and pressures and with reactants preheating can be realized with confidence. With a better thermal insulation, they will improve H$_2$ efficiency.

In order to validate the multi-fuel potential of the proposed technology, complementary tests with other fuels (natural gas, diesel fuel and ester vegetable oil) are scheduled within the first quarter of 2003. Then, the HSR reactor will be complemented by the addition of catalytic reactors for CO to CO$_2$ conversion and will be coupled with a PEMFC. The efficiency of the whole system will be evaluated at that time.

Acknowledgements

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