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# Use of non-thermal plasma for hydrocarbon reforming

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**Abstract**

Fuel cell systems for automotive applications are nowadays an important research activity. No infrastructure for distributing hydrogen still exists and the research efforts are thus focused on on-board hydrogen generation from hydrocarbon reforming. Experimental catalytic reformers have already been developed but their cost, their low time of life due to sulphur and carbon pollution problems make these reformers unusable for a commercial application. This paper presents a non-thermal gliding arc system designed to convert gasoline into hydrogen-rich gas in auto-thermal or steam reforming conditions for car application. In a first part, the chemistry of hydrocarbon reforming is briefly explained. The technology and design of the plasma reactor composed of two gliding arc in series is detailed in a second part. Finally, we demonstrate the feasibility of producing hydrogen in both auto-thermal and steam reforming conditions. The attention is focused on the influence of the different operating parameters (pressure, temperature, air and steam ratio, inlet flow rates) on the reformer efficiency and the composition of the produced gas. The experimental results are then compared to the performances of other non-thermal plasma reformers. This new plasma reformer is at its first stage of development and several technological optimisations can be performed to improve its chemical efficiency.

*Keywords:* Auto-thermal reforming; Steam reforming; Gasoline; Hydrogen; Plasma; Gliding arc

## 1. Introduction

The increasing concern in environmental and pollution problems implied a large amount of efforts in the scientific world to develop alternative and renewable technologies for energy and electricity production. The fossil fuels are the major source of energy but the burning fuel technologies induce the emission of a large amount of carbon and nitrogen oxides responsible of the greenhouse effect. The growing energy consumption and the environment preservation imply to develop cleaner and more efficient energy production systems.

The fuel cell technology is nowadays very promising to respond to this energy need, especially in transport application. Fuel cells generate electricity by converting oxygen and hydrogen into water without combustion. One of the main problems concerning the fuel cell systems is the use of hydrogen. Pure hydrogen can be used: it would be possible to store hydrogen in a car but the storage of hydrogen is very expensive and the hydrogen infrastructures do not exist. In this context, all the major international car companies consider that, at least at short middle term, an intermediate state for the development of fuel cells in automotive applications will be possible by producing hydrogen directly from gasoline since the infrastructure for gasoline distribution already exists. This process called fuel reforming is already used for static production of hydrogen for different chemical processes (production of ammoniac and methanol for example).

Several catalytic reformers have been developed for fuel reforming: these reformers present however some problems. Using conventional gasoline, the catalysers are contaminated rapidly by sulphur contained in the fuel or by carbon deposit. They are moreover very expensive and their time of life is relatively short. Finally, the start-up time is too long (several minutes) for an automotive application.

The plasma technology could be very interesting to reform fuel for hydrogen production and eliminate then the problems encountered in the catalytic reformers. The role of catalysers in the reforming process is to create radical species enhanc-

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ing the reaction. The role of plasma would be then to provide the energy and to create free radicals needed for fuel reforming. The catalytic effect of non-thermal plasma to produce hydrogen has already been demonstrated in several papers [1–8].

The aim of the work presented in this paper was to develop a flexible and reliable non-thermal plasma prototype able to reform gasoline in auto-thermal and steam reforming conditions in a large range of fuel flow rate. The technology chosen for the development of this reactor is based on the gliding arc system [9–15].

In a first part, the chemistry implied in plasma reforming is briefly explained. The gliding arc plasma technology and the properties of this discharge are presented in a second part. The design and development of the gliding arc reactor and its power supply are detailed in a third part. The fourth and last part describes the experimental and quantitative results obtained in auto-thermal and steam reforming conditions: we can then demonstrate the catalytic effect of the gliding discharge on the chemical reactions.

## 2. Gasoline reforming chemistry

This part is a brief summary of the chemical reactions implied in the current plasma process. A detailed description of the gasoline reforming chemistry can be found in references [16–19].

This plasma process uses the auto-thermal reforming of gasoline for the production of a hydrogen-rich gas. The auto-thermal reforming process is the combination of the partial oxidation and steam reforming reactions. Fuel is mixed to hot air and water steam: the energy released by the partial oxidation of fuel is then used to activate the steam reforming reaction. In conventional reactors, the ratio $H_2O/C_nH_m$ is usually higher than the stoichiometric one, the excess of water can be used to convert CO, in a second reactor, into hydrogen by using the water-shift reaction. The auto-thermal reforming can work with or without catalysers but the use of catalysers allows to work at lower temperature and to avoid the production of carbon soot.

## 3. Non-thermal technologies: state of the art

### 3.1. Advantages of non-thermal plasma technology

The aim of the plasma is to play a catalytic role by creating reactive species needed for the different chemical reactions.

Several different plasma reactors have already been developed in different research groups to reform hydrocarbons by partial oxidation or auto-thermal reforming [1–8,14–15,20]. Only few plasma reactors have however been developed for steam reforming of hydrocarbons [6,7,20]. Among the different plasma characteristics, we can distinguish two main categories: thermal plasma and non-thermal plasma.

For thermal plasma, the electrical power injected in the discharge is high (higher than 1 kW) and the neutral species and the electrons have then the same temperature (around 5000–10,000 K). The temperature in the reactor and the energy consumption are thus very high and the cooling of the electrodes is generally useful to reduce their thermal erosion. The use of this technology is therefore not relevant in fuel cell application for an efficient production of hydrogen in terms of energy consumption.

For non-thermal plasma, the electrical power is very low (few hundreds watts): the temperature of neutral species does not change whereas the temperature of electrons is very high (up to 5000 K). In this case, the role of the plasma is not to provide energy to the system but to generate radical and excited species allowing initiating and enhancing the chemical reactions. The advantages of using non-thermal plasma are related to the lower temperature that will result in lower energy consumption and lower electrode erosion since the cooling of the electrodes is generally not necessary. In addition, the size and weight of the non-thermal plasma reactors are relatively low, which is very attractive for mobile applications.

### 3.2. The existing technologies

Different non-thermal plasma technologies that have been reported in literature have already been used for the reforming of hydrocarbons: the corona discharge [5], the microwave plasma [6], the dielectric barrier discharge (DBD) [21] and the gliding arc technology [8,14,15,20]. The main issue for creating non-equilibrium plasma is to control the current intensity and the power of the discharge. We can control these parameters by acting on the power supply, flow rate and design. All these parameters are strongly related. Two ways are possible to create non-thermal plasma:

- using a static discharge, as it is the case for corona discharge or DBD;
- using a dynamic discharge which is pushed by the gas flow along the reactor; this technique has been used in the gliding arc and microwave technologies.

### 3.3. The gliding arc technology

The gliding arc technology is one of the most relevant techniques for on-board application and hydrogen production. This technology is not complex and presents a high flexibility allowing to work in a high range of flow rates and to treat a large amount of chemical species. The main advantage of this device is that we can easily vary the power in the discharge, by acting on the device of the electrode, and on the voltage level. This reactor can work with a direct or alternative voltage and the power supply technology is then less complex than for a corona discharge or a microwave plasma reactor.

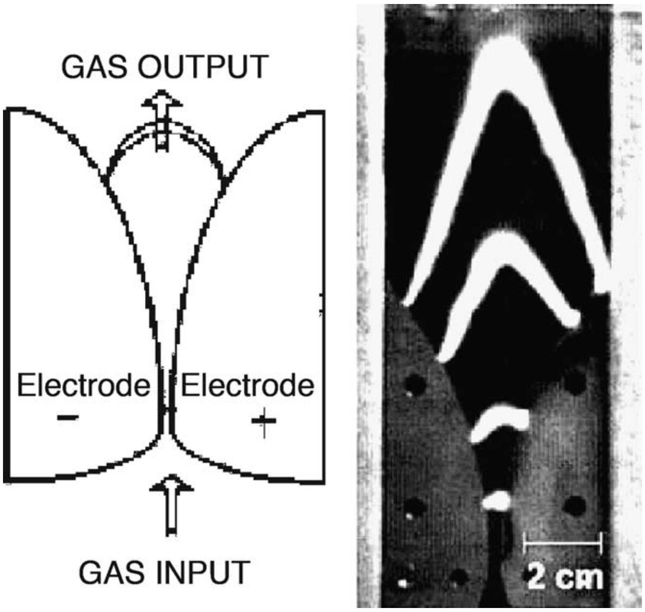

Fig. 1. Design of a gliding arc reactor [10].

From this analysis, it has been decided to develop a system based on the gliding arc technology. The gliding arc has been especially used to treat gas pollutants, for gas conversions (especially steam reforming of methane to produce synthesis gas [20]), and other several chemical processes. A similar technology has already been used by Czernichowski and co-workers [15] and Bromberg et al. [1–3,8]. In the first case, the reactor consists of two thin diverging electrodes and the gas is introduced at the bottom of these electrodes (Fig. 1). A high voltage is applied between these two electrodes and an arc is then created between the horns. This arc is pushed by the rising gas, moves upward and is switched off at the end of the electrodes [9–12]. Another discharge is then created at the back of the electrodes. Fig. 1 shows the moving discharge along the electrodes. In the technology developed by MIT [8], the non-thermal discharge is generated between a central electrode and an external conical shape.

## 4. Experimental set-up

### 4.1. The experimental conditions

The plasma reformer presented in this paper has been designed and developed to work in auto-thermal or steam reforming conditions for pressures up to $3 \times 10^5$ Pa and temperatures up to 773 K. The working specifications of the plasma reformer are summarised in Table 1. The important technological innovation is that the plasma reactor allows working for pressure up to $3 \times 10^5$ Pa whereas only a few non-thermal plasma reactors have been developed to work above $1 \times 10^5$ Pa [22]. This reactor has been designed especially for the reforming of gasoline. The hydrocarbon used is a non-sulphur synthetic gasoline (California gasoline—Syntroleum) with the following average formula: $C_7H_{15.2}$. It has been treated for air ratios between 0.1 and 0.4 and steam ratios between 1 and 3 in auto-thermal conditions and for steam ratios between 1 and 5 in steam reforming conditions.

Table 1
Operating conditions of the plasma reformer

| Fuel | Non-sulphur synthetic gasoline (California gasoline—Syntroleum)[a] |
|---|---|
| Input thermal fuel power | 10–40 kW |
| Maximum pressure | $3 \times 10^5$ Pa |
| Inlet temperature | 773 K |
| Oxidants | Water and air |
| Air flow (air ratio: 0.1–0.25) | 15–106 g min$^{-1}$ |
| Water flow (steam/carbon ratio: 1–5) | 12–85 g min$^{-1}$ |

[a] $C_7H_{15.2}$, molar mass: 100.39 g mol$^{-1}$; LHV = 4430 kJ mol$^{-1}$.

### 4.2. The plasma reactor

The gliding arc reactor developed for fuel reforming is composed of the following parts (Fig. 2):

- A stainless-steel vessel with a volume of 6.3 l. This vessel allows working for pressures up to $3 \times 10^5$ Pa, to mechanically maintain the electrode supports and the injection system and to vary easily the reaction and discharge volume. It contains a borosilicate window in order to observe the discharge.
- The injection system: a mixture of air, water and fuel can be injected in the reactor with a temperature up to 773 K and a pressure up to $3 \times 10^5$ Pa. Fuel and water steams are mixed before entering the reactor and injected via a stainless-steel tube. Fuel is then vaporised before the entrance in the plasma reactor. The inner diameter of the stainless steel tube is 4 mm. Hot air is injected separately through six holes of 3 mm diameter located around the steam injection tube. This injection system creates high velocities for hot air and the mixture fuel-water, up to 80 m s$^{-1}$. We can then reach easily the non-thermal regime of the gliding arc, as demonstrated by Mutaf-Yardimci et al. [11]. The residence time in the plasma and reaction chambers has not been evaluated accurately but it varies between 3 and 12 ms.
- Two sets of electrodes allow working with two gliding arcs in series. The gliding arc electrodes are composed of tungsten with an ellipsoidal geometry to increase the length of the discharge along these electrodes. This system allows to treat a maximum volume in the discharge and then to increase the efficiency of the system. The electrodes are 45 mm length, 20 mm height and 2 mm width.
- The electrode supports: they allow connecting the electrodes to the power supply, maintaining them inside the reactor and adjusting the distance between the anode and the cathode. The ignition of the discharge is actually strongly dependent on the pressure and temperature: it is thus very

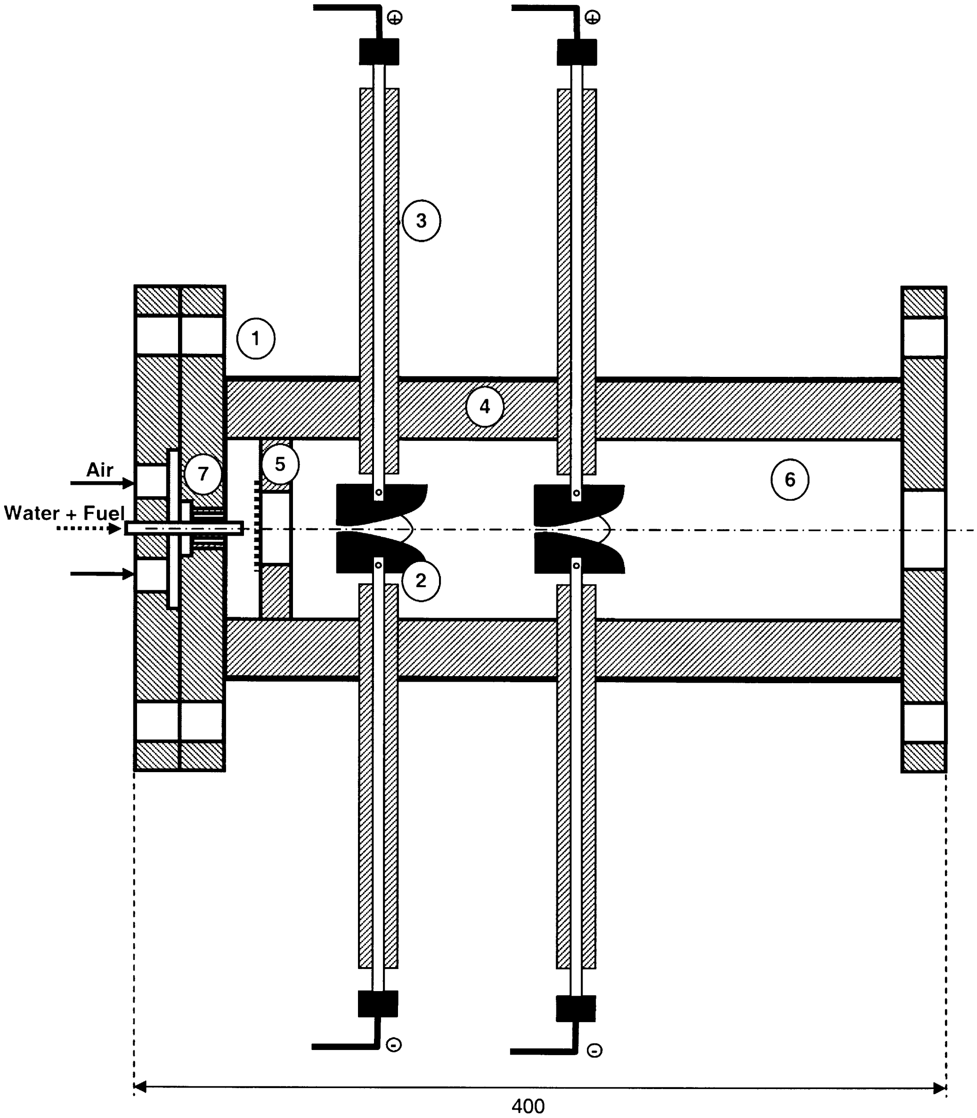

Fig. 2. Design of the plasma reactor: (1) stainless-steel vessel, (2) electrodes, (3) electrode supports, (4) inner thermal insulation, (5) flame guide, (6) post-discharge chamber, (7) injection system.

important to vary accurately the distance between the electrodes in order to further the discharge. The electrical connections are composed of an external ceramic tube ($Al_2O_3/SiO_2$) and an internal Inconel tube. Two sets of seals and fittings are used for sealing and mechanical rigidity. The function of the ceramic tube is to realise a thermal and electrical insulation for the electrode support.

- The inner thermal insulation ($Al_2O_3/SiO_2$) placed inside the stainless-steel vessel.

### 4.3. *The power supply*

The specifications of the power supply of the plasma reactor are presented in Table 2. This new power supply is composed of two high voltage systems, for each set of electrodes. It allows working in ac or dc configurations for both gliding arc systems. The first high voltage system creates a maximum potential difference equal to 5000 V whereas this difference is equal to 10,000 V for the second system. The electric designs of the secondary circuits for the two systems in ac and dc configurations are shown in Fig. 3.

Each high voltage power supply uses two high voltage transformers which are connected on the primary circuit to 220 V/50 Hz. Each transformer delivers an alternating volt-

Table 2
Specifications of the power supply

| Electric input | 220 V/50 Hz, 6 kW | |
|---|---|---|
| | First high voltage system | Second high voltage system |
| High voltage | ±2500 V | ±5000 V |
| Electric power | 2 kW | 4 kW |
| Electric signals | ac (50 Hz) or dc | ac (50 Hz) or dc |
| Maximum electric current | 400 mA | 450 mA |

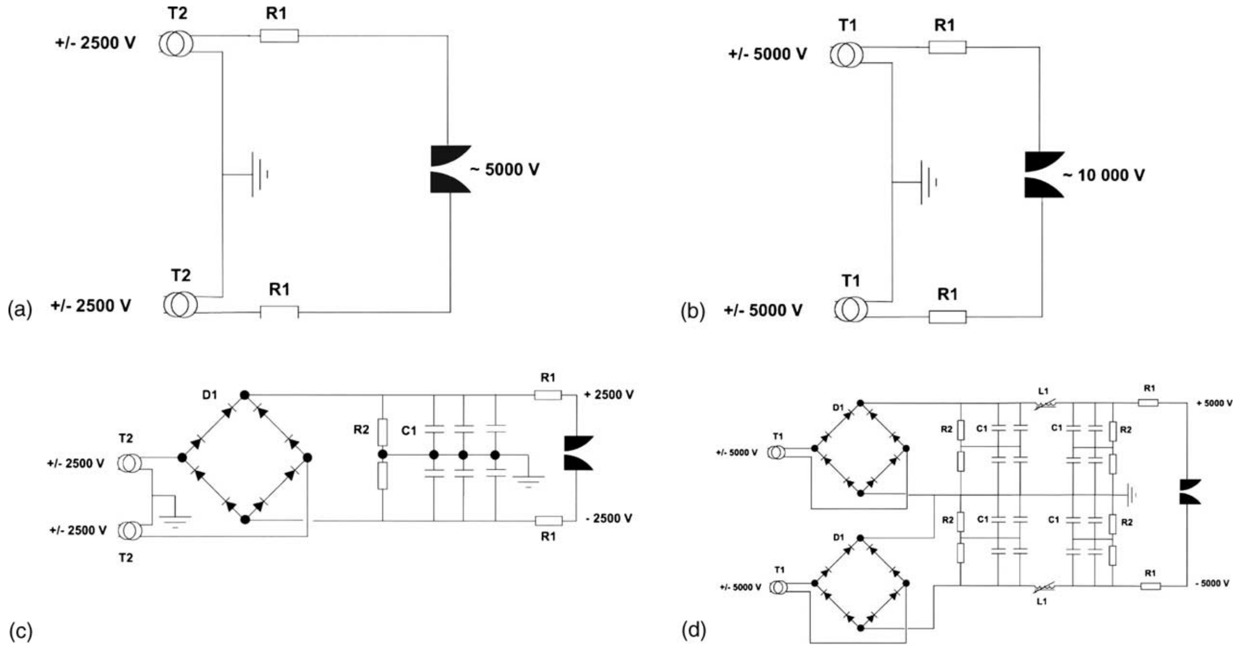

Fig. 3. Electric schemes of the power supply: (a) ac, ±2500 V; (b) ac, ±5000 V; (c) dc, ±2500 V; (d) dc, ±5000 V.

age (±2500 or ±5000 V). In order to run in ac configuration the two high voltage transformers are connected directly to power resistances. The power resistances are used to control the electric current in the power supply and then keep a non-thermal state in the gliding discharge. The high voltage transformers have been built to have adjustable leakage fluxes: these leakage fluxes are a second way to control the current in the secondary electric part.

In dc configurations, the superposition of diode bridges and high voltage capacities allows to create a direct voltage difference between the electrodes.

## 5. Results and discussion

### 5.1. The physical properties of the gliding arc reactor

The plasma reactor has been tested under the specifications defined in Table 1 in dc and ac configuration for the two power supplies.

The plasma reactor presents the following characteristics:

- Instantaneous and good ignition of the two gliding arcs up to $3 \times 10^5$ Pa.
- Continuous run for several hours without damages in autothermal and steam reforming conditions.
- Stability of the two gliding arcs for pressures between 1 and $3 \times 10^5$ Pa.
- No electric interaction and disturbance between the two gliding arc systems.
- High tolerance to carbon deposit and sulphur content: the plasma reactor works very well, with no extinction, even if carbon is produced inside the reactor. It has been tested during several hours and without damages or extinction with $C_7H_{15.2}$ fuel, and French Gasoline 95.
- Low electrode erosion: we have observed a very weak erosion of the electrodes. The thermo-mechanical properties of the electrodes are however much better in ac configuration. In dc configuration, the erosion is not homogeneous on the two electrodes: the anode is much more eroded than the cathode. The ac configuration is thus more convenient and the quantitative results are the same for the two configurations.

The best configuration to have a stable and non-thermal plasma discharge for temperature up to 773 K and pressure up to $3 \times 10^5$ Pa is to work with an inter-electrode gap, for the two sets of electrode, equal to 2 mm and in ac configuration. Fig. 4 shows the gliding discharge on the first set of electrodes, in ac configuration and in a mixture of hot air and water steam at $2 \times 10^5$ Pa and 573 K.

### 5.2. The chemical efficiency of the gliding discharge reactor

#### 5.2.1. Evaluation of the plasma reformer efficiency

The reformer efficiency is defined as the energy present in hydrogen at the output of the reactor versus the input energy coming from fuel. We assume that carbon monoxide will be converted in hydrogen in a second water-shift stage. The reformer efficiency is then calculated with the following relation:

$$\eta_{\mathrm{ref}} = \frac{(\dot{n}_{\mathrm{CO}} + \dot{n}_{\mathrm{H_2}})\Delta H_{\mathrm{H_2}}}{\dot{n}_{\mathrm{fuel}}\Delta \mathrm{H}_{\mathrm{fuel}} + P_{\mathrm{elec}}} \qquad (1)$$

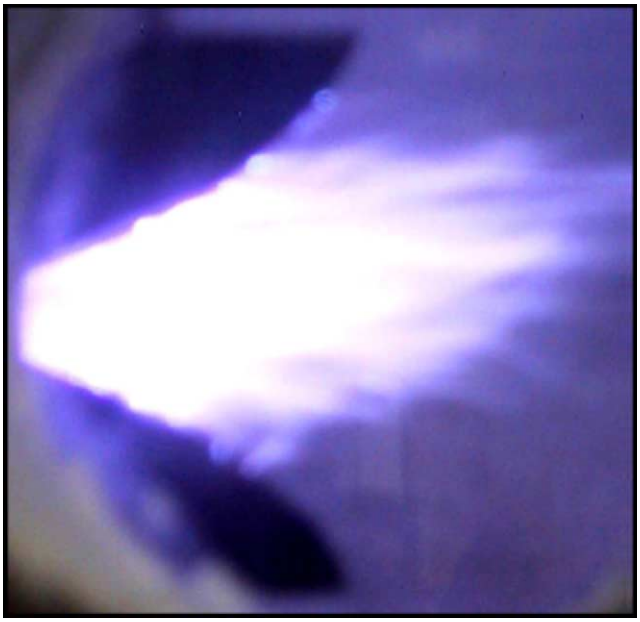

Fig. 4. The gliding discharge in hot air and water (temperature: 573 K, pressure: $2 \times 10^5$ Pa).

with $\dot{n}_{H_2}$ the hydrogen molar flux emitted by the plasma reactor, $\dot{n}_{CO}$ the carbon monoxide molar flux emitted by the plasma reactor, $\dot{n}_{fuel}$ the input gasoline flux, $\Delta H_{H_2}$ the lower heat of combustion for hydrogen, $\Delta H_{fuel}$ the lower heat of combustion for gasoline, and $P_{elec}$ the electric power provided to the gas by the plasma discharge.

The maximum electric power provided to the gas by the two plasma discharges has been evaluated, equal to 1000 W (500 W per discharge). The electrical characterizations have been carried out using a numerical oscilloscope (HP 54615B) connected to a PC for the data storage. The data acquisition was controlled by the software HP-Vee. The high voltage between the electrodes was measured using a high voltage probe (Elditest, GE3830, maximum voltage: 30 kV) connected to the oscilloscope. The electric current in the high voltage was carried out by measuring the voltage, with the high voltage probe, across a 10 Ω resistance placed between one electrode and the secondary electric circuit.

The conversion rate allows finally evaluating the amount of input gasoline which has been converted in $H_2$, CO, $CO_2$ or light hydrocarbons in the plasma reactor. It is evaluated using the following equation:

$$U_{gasoline} = \frac{\dot{n}_{C,dry,out}}{\dot{n}_{C,in}} = \frac{\dot{n}_{CO,dry} + \dot{n}_{CO_2,dry} + \dot{n}_{CH_4,dry}}{7\dot{n}_{C_7H_{15,2}}} \quad (2)$$

with $\dot{n}_{C_7H_{15,2}} = \dot{n}_{gasoline,in}$ as gasoline flux.

The molar fluxes are calculated by measuring the volume flow of dry gas at the output (using a gas meter Ritter LG 50) and the product ratio of the different elements ($H_2$, CO, $CO_2$, $CH_4$ and total hydrocarbon concentrations). The hydrogen ratio is measured using a Hydros 100 thermal conductivity analyser-Rosemount. CO and $CO_2$ ratios are determined with a Binos 100 dual Channel Infrared Photometer-Rosemount. A FID analyser (Model 109—JUM Engineering) allows measuring the product ratios of total hydrocarbons and methane. The output gas is dried after the plasma reactor and the analytic equipment measures thus a dry gas concentration.

The molar fluxes are then determined according to the relation:

$$\dot{n}_i = \left( \frac{\dot{V}_{exhaust\,gas,standard,\,dry}}{V_{ms}} \right) \times x_i \quad (3)$$

with $\dot{n}_i$ the product flux of component $i$, $x_i$ the product ratio of component $i$ measured by the analysers, $V_{ms}$ the molar standard volume of the ideal gas, $V_{exhaust,\,standart,\,dry}$ the dry gas volume measured at the output in standard conditions.

The quantity of air injected in the reactor is defined using the air ratio $\alpha$. The air ratio corresponds to the ratio between the amount of injected oxygen coming from air and the amount of oxygen needed for a total combustion of fuel. For the fuel used here, we have:

$$\text{Total combustion:} \quad C_7H_{15.2} + 10.8O_2 \rightarrow 7CO_2 + 7.6H_2O$$

$$\text{Partial oxidation :} \quad C_7H_{15.2} + zO_2 \rightarrow xCO + yH_2$$

The air ratio $\alpha$ is then defined as: $\alpha = z/10.8$.

The quantity of water injected in the reactor is defined by the steam ratio S/C. This steam ratio is the moles number of water divided by the moles number of carbon coming from fuel. For this fuel, we have: S/C = moles (water)/7 × moles (fuel).

### *5.2.2. The experimental results*

*5.2.2.1. Auto-thermal reforming.* The first set of experiments has been conducted in auto-thermal conditions with a fuel input power equal to 10 kW. The different experimental results are summarised in Table 3. The highest hydrogen concentration has been obtained for a steam ratio equal to 2.5. Fig. 5 shows the evolution of the concentration of the different elements in the dry gas according to the air ratio for a steam ratio equal to 2.5. The maximum hydrogen yield is obtained for an air ratio equal to 0.1 and is equal to 7%, whereas the carbon monoxide ratio is equal to 3.7%. The hydrogen concentration decreases as the air ratio increases. This can be in part due to the dilution effect of nitrogen (since air is used as oxidant). We can observe the production of a high amount of methane: its concentration is then equal 9.2% for an air ratio equal to 0.1 and decreases up to 4% for air ratio equal to 0.4. The carbon monoxide and carbon dioxide concentrations present however the reverse feature and reaches a maximum respectively equal to 11 and 2% for an air ratio equal to 0.4. This is mainly explained by the increase of the conversion rate with the air ratio (Fig. 6). The reformer efficiency changes with the same tendencies as the CO concentration and increases also with the air ratio up to 12.3% for an air ratio equal to 0.4 (Fig. 7). The increase of the reformer efficiency and the conversion rate are directly related to the higher temperature working with a high air ratio

Table 3
Summary of the experimental results obtained in auto-thermal and steam reforming conditions

| Input data | | | | Output data | | | | |
|---|---|---|---|---|---|---|---|---|
| Fuel flow (kW) | Pressure ($\times 10^5$ Pa) | Air ratio | S/C | $H_2$ | CO | $CO_2$ | $CH_4$ | Reformer efficiency |
| 10 | 2 | 0.1 | 2.5 | 6.6 | 3.7 | 1 | 9.2 | 2.2 |
| 10 | 2 | 0.2 | 2.5 | 2.6 | 2.4 | 1.1 | 8.2 | 2.3 |
| 10 | 2 | 0.33 | 2.5 | 1.1 | 6.8 | 1.6 | 7.2 | 5.5 |
| 10 | 2 | 0.4 | 2.5 | 1 | 11.1 | 1.8 | 3.7 | 12.3 |
| 10 | 1.3 | 0.2 | 2.5 | 2.7 | 2.7 | 0.6 | 3.7 | 3 |
| 10 | 2.5 | 0.2 | 2.5 | 1.9 | 12 | 1.5 | 5.5 | 8 |
| 10 | 1 | – | 1 | 27 | 18 | 1 | – | 28 |
| 10 | 1 | – | 2 | 27 | 15 | 2 | – | 27 |
| 10 | 1 | – | 3 | 30 | 17 | 3 | – | 26 |
| 10 | 1 | – | 4 | 31 | 16 | 3 | – | 23.5 |
| 10 | 1 | – | 5 | 31 | 15 | 4 | – | 29 |
| 7 | 1 | – | 3 | 28.7 | 15 | 3 | 40 | 28 |
| 11 | 1 | – | 3 | 29.2 | 16 | 3 | 40 | 18 |
| 15 | 1 | – | 3 | 27.8 | 16 | 3 | 40 | 15.5 |
| 18 | 1 | – | 3 | 27.7 | 15 | 3 | 40 | 10 |

[17,27]. Ersoz et al. [25] have theoretically shown that there is a maximum efficiency for a temperature equal to around 973 K.

Fig. 8 highlights the influence of the pressure on the reformer efficiency. We can see that the reformer efficiency increases drastically with pressure: it is equal to 8% at $2.5 \times 10^5$ Pa (air ratio = 0.2, S/C = 2.5) and is thus multiplied by a factor higher than 2 from $2 \times 10^5$ to $2.5 \times 10^5$ Pa. As a consequence, we can increase significantly the hydrogen yield and the reformer efficiency by working at a pressure three times higher than the atmospheric pressure. We could then reach a maximum reformer efficiency equal to around 27% at $2.5 \times 10^5$ Pa, for an air ratio, steam ratio, inlet temperature and fuel power respectively equal to 0.4, 2.5, 773 K and 10 kW. It has been demonstrated by electric measurements that the increase of the operating pressure induces an increase of the time between two discharges, without changing the level of voltage and current. This characteristic should have a negative effect on the reformer efficiency. However, by increasing the pressure, we increase also the resident time of the gas inside the discharge: this effect seems to counterbalance the previous one and further the hydrogen production.

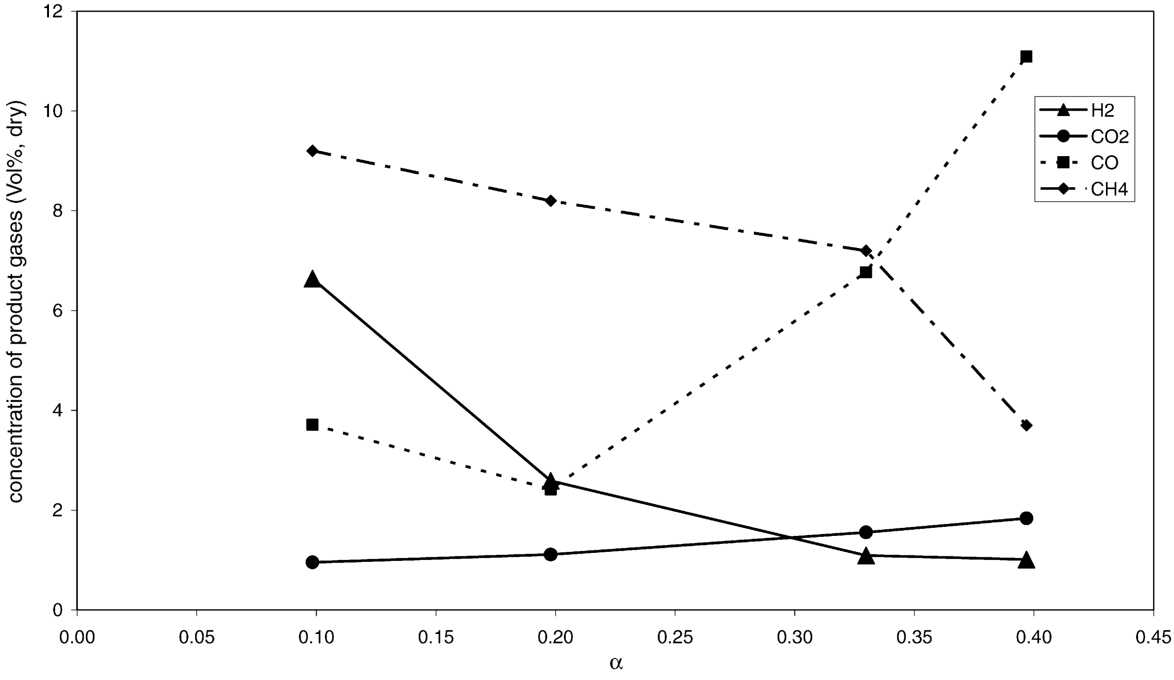

Fig. 5. Evolution of the composition of the dry output gas produced in auto-thermal reforming conditions as a function of the air ratio (fuel power: 10 kW, S/C: 2.5, inlet temperature: 773 K, pressure: $2 \times 10^5$ Pa).

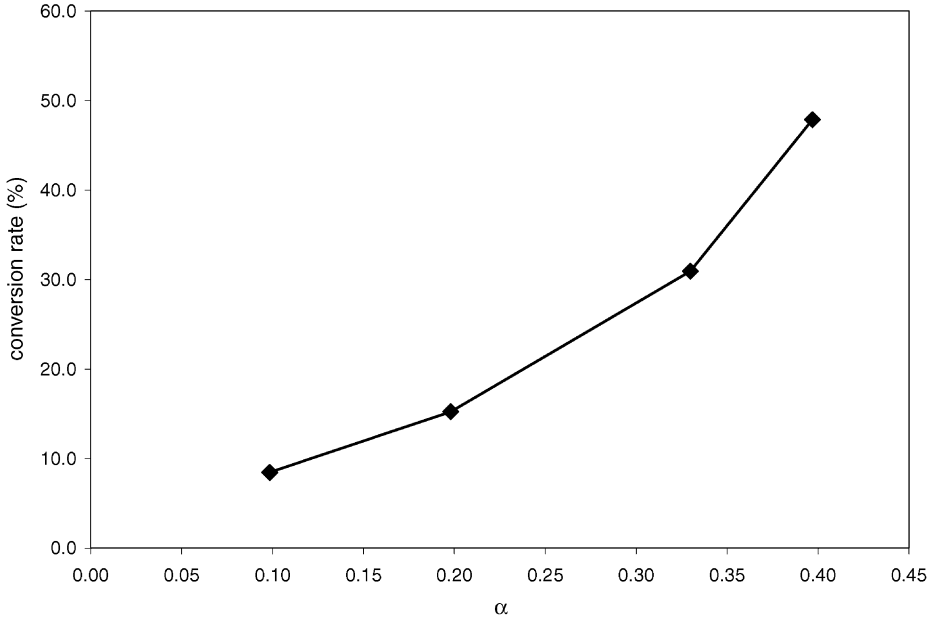

Fig. 6. Evolution of the conversion rate in auto-thermal reforming conditions as a function of the air ratio (fuel power: 10 kW, S/C: 2.5, inlet temperature: 773 K, pressure: $2 \times 10^5$ Pa).

These results show the feasibility of producing hydrogen in auto-thermal conditions using the gliding discharge technology. No carbon soot production has been observed during the different tests in auto-thermal reforming conditions.

*5.2.2.2. Steam reforming.* In a second set of experiments, the plasma reactor has been tested in steam reforming conditions. Fig. 9 shows the evolution of the concentration of the different elements according to the steam ratio, for a fuel power equal to 10 kW. We can notice a slight increase of $H_2$ and $CO_2$ concentrations with S/C whereas CO concentration decreases. The increase of water content seems therefore to further the water-shift conversion of CO into $H_2$ and $CO_2$. The hydrogen concentration reaches a level equal to 30% for a steam ratio equal to 3. If we consider that all carbon monoxide will be converted in hydrogen in a second water-shift reactor, the total hydrogen concentration is then equal to 47%.

The conversion rate and the reformer efficiency (Figs. 10 and 11) do not strongly vary with the steam ratio and are respectively equal to 57 and 26% for S/C equal to 3. Fig. 12 presents the evolution of the reformer efficiency

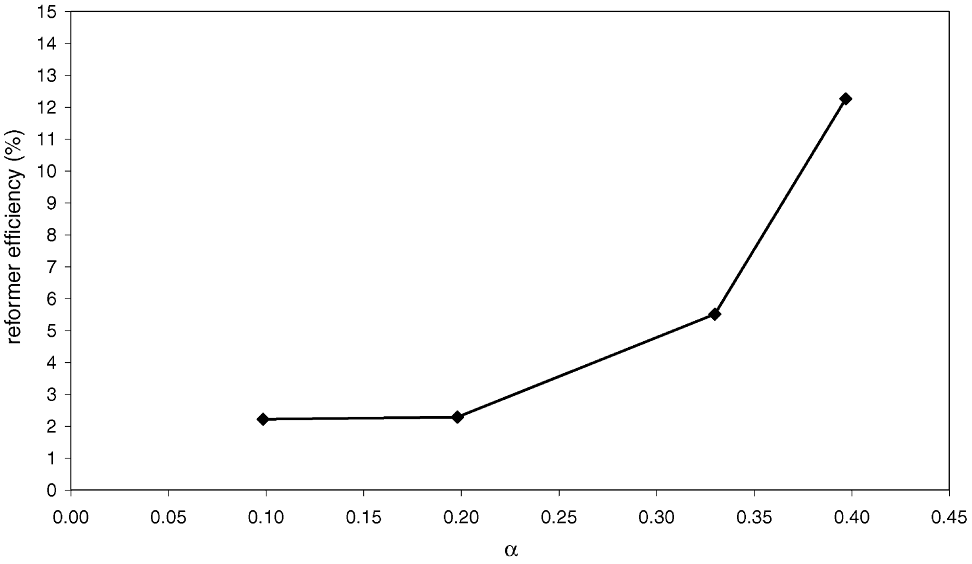

Fig. 7. Evolution of the reformer efficiency in auto-thermal reforming conditions as a function of the air ratio (fuel power: 10 kW, S/C: 2.5, inlet temperature: 773 K, pressure: $2 \times 10^5$ Pa).

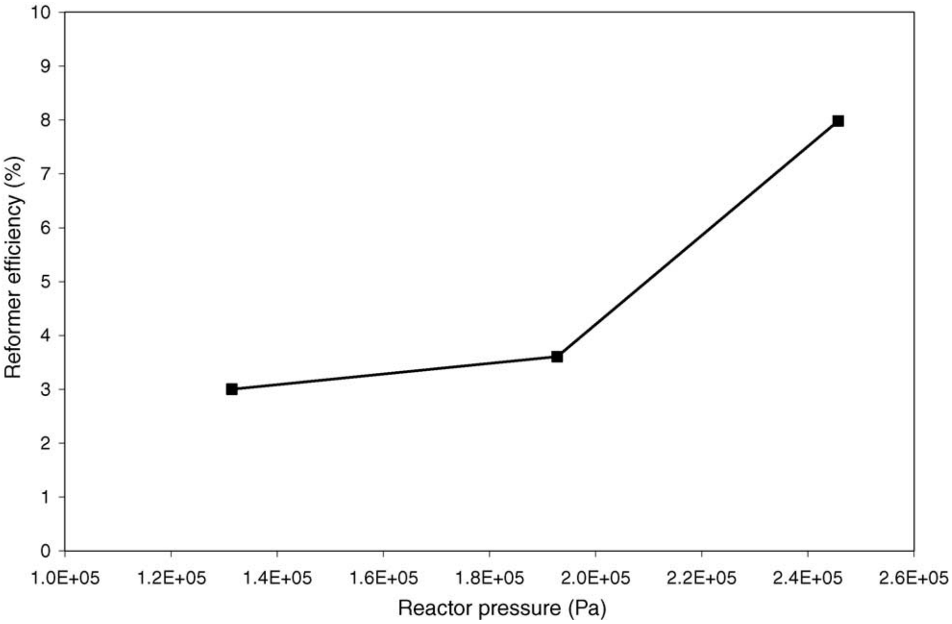

Fig. 8. Evolution of the reformer efficiency in auto-thermal reforming conditions as a function of the pressure (fuel power: 10 kW, S/C: 2.5, inlet temperature: 773 K, air ratio: 0.2).

according to the gasoline heat flow for a steam ratio equal to 3. This efficiency decreases drastically when the fuel power increases. This is especially due to the fact that the increasing of fuel power increases the inlet velocities of the gas and then decreases the resident time of the gas in the plasma reactor.

The level of produced hydrocarbons heavier than methane is higher than 10%. No carbon production has been observed during the different tests in steam reforming conditions. The concentration of methane produced during steam reforming is however very high, equal to 40%. This second tests of experiments demonstrates the catalytic effect of the gliding discharge in steam reforming conditions.

## 6. Comparison with the other technologies and optimisations

The feasibility to produce hydrogen in auto-thermal and steam reforming conditions has been demonstrated. Tables 4 and 5 show the experimental results obtained with

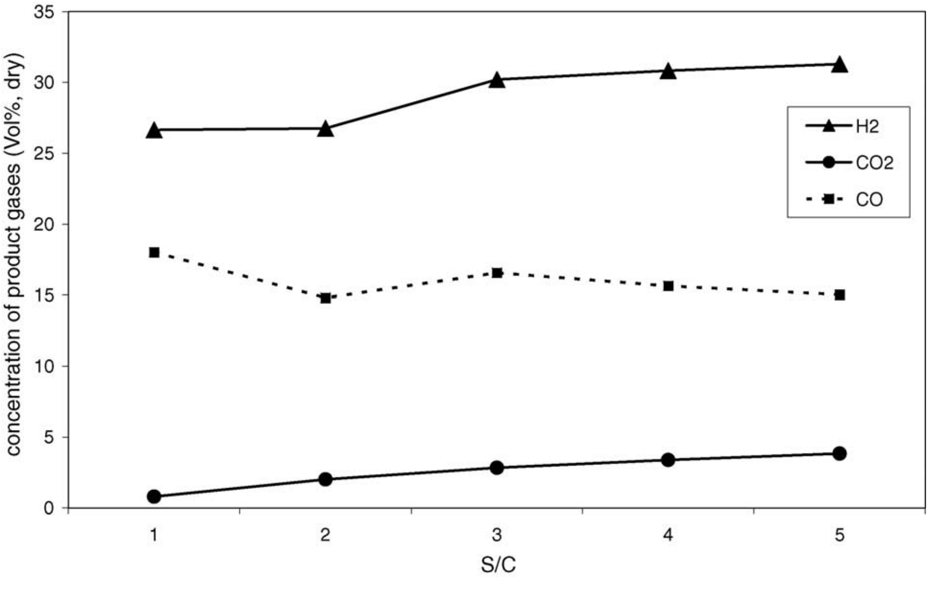

Fig. 9. Evolution of the composition of the dry output gas produced in steam reforming conditions as a function of the steam ratio (fuel power: 10 kW, inlet temperature: 773 K, pressure: $1 \times 10^5$ Pa).

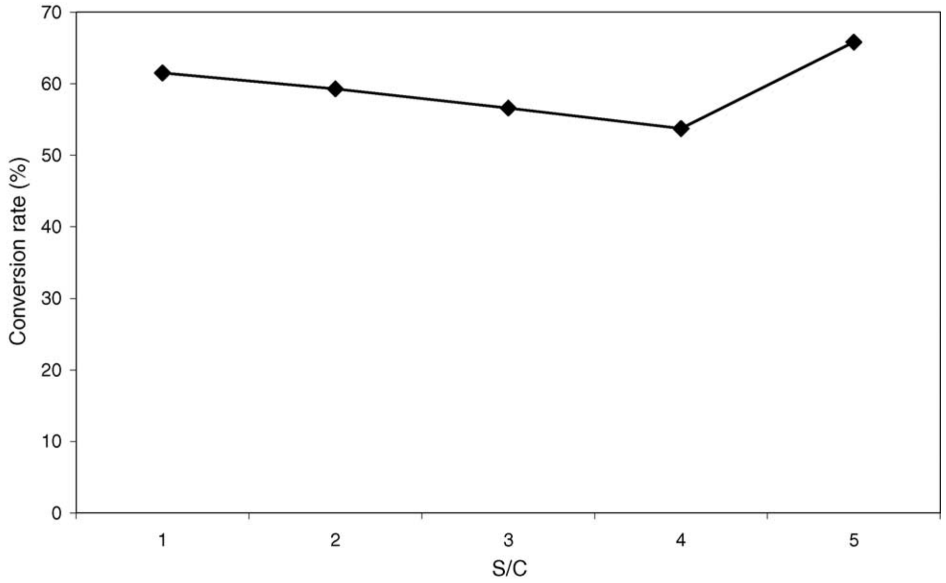

Fig. 10. Evolution of the conversion rate in steam reforming conditions as a function of the steam ratio (fuel power: 10 kW, inlet temperature: 773 K, pressure: $1 \times 10^5$ Pa).

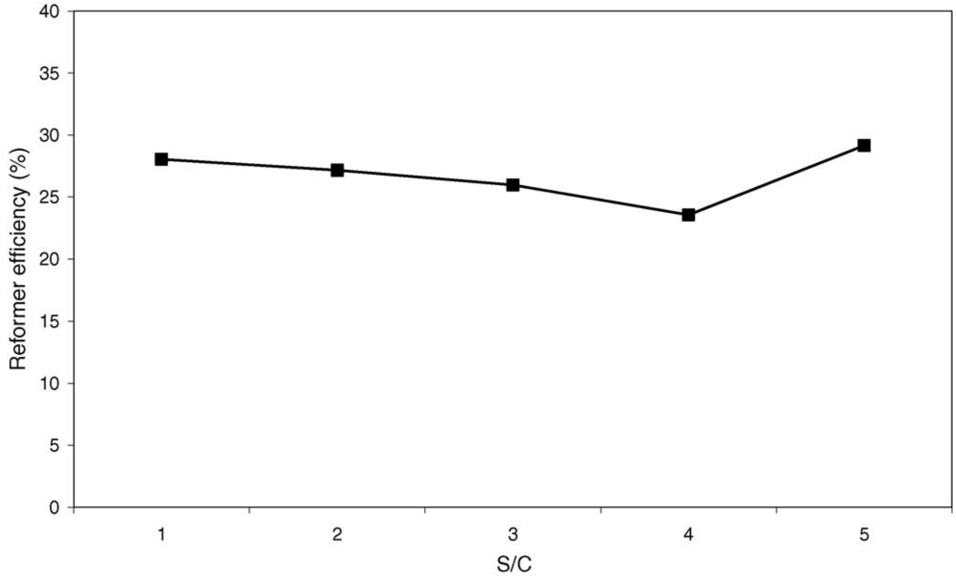

Fig. 11. Evolution of the reformer efficiency in steam reforming conditions as a function of the steam ratio (fuel power: 10 kW, inlet temperature: 773 K, pressure: $1 \times 10^5$ Pa).

Table 4
Chemical efficiency of several plasma reformers (ATR: auto-thermal reforming, POX: partial oxidation, STR: steam reforming)

| Technology | Hydrocarbon | Experimental conditions | | | | | Products concentration (dry vol.%) | | | | Reformate temperature (K) | $\eta$ (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Chemical reaction | Air ratio | S/C | Fuel power (kW) | Absolute pressure ($\times 10^5$ Pa) | $H_2$ | CO | $CO_2$ | $CH_4$ | | | |
| Gliding arc non-thermal | Diesel | ATR | 0.4 | 1.8 | 1 | 1 | 23 | 17 | 6.2 | 1.2 | 1000–1300 | 85 | [8] |
| Corona discharge + catalyst | Isooctane | ATR | 0.28 | 1 | 0.02 | 1 | 46 | 16 | 16 | – | 900–1100 | 55 | [5] |
| Gliding arc thermal | Isooctane | POX | 0.25 | – | 14 | 1 | 22 | 15 | 2 | 3 | 1200 | 9 | [3] |
| Gliding arc thermal | Diesel | POX | 0.25 | – | 17 | 1 | 23.5 | 23 | 0.1 | 0.03 | 1200 | 9 | [3] |
| Microwave | Hexane | STR | – | 2 | 1.5–4 | 1 | 66 | 25 | 4 | – | ? | ? | [6] |

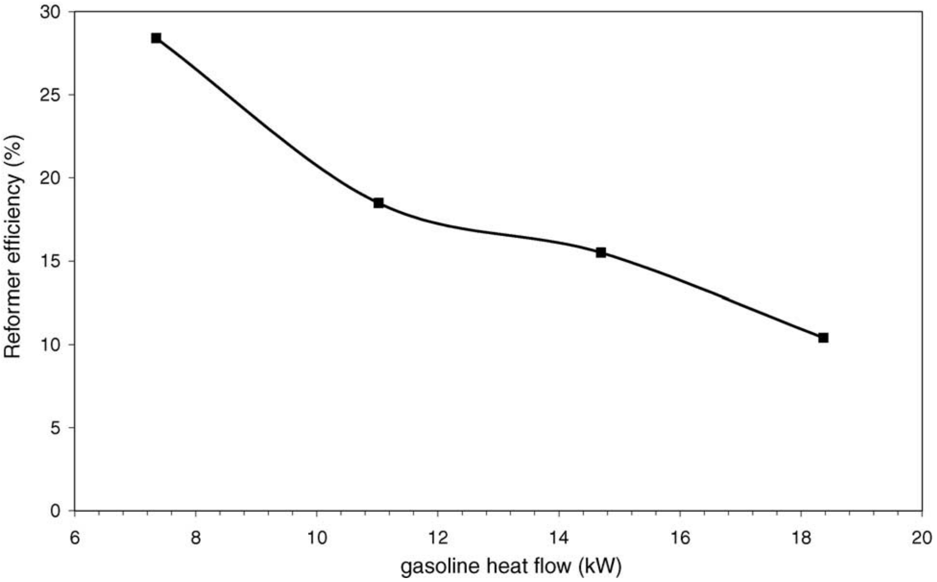

Fig. 12. Evolution of the reformer efficiency in steam reforming conditions as a function of the input fuel power (S/C: 3, inlet temperature: 773 K, pressure: $1 \times 10^5$ Pa).

different other plasma and catalytic reformers. We can see that the preliminary results of the plasma reactor developed here are lower than the previous plasma reactors. The hydrogen yield and reformer efficiency are then respectively around three times and six times lower than the non-thermal plasma reformer developed by Bromberg et al. [8] in auto-thermal conditions. The main difference in the operating conditions is that the temperature used for the other plasma reactors is 1000 K or higher, which is 300 K higher than the current plasma reactor. These non-thermal plasma reactors work at atmospheric pressure and for fuel power twice to tenth lower than this one. In steam reforming conditions, the chemistry in the plasma reactor seems to be very different from the catalytic reactors where the concentration of hydrogen and methane are respectively equal to around 70 and 4% [23,24]. The main reason may be due to the fact that the chemical reactions in the catalytic reactors are heterogeneous whereas they occur in the gas and plasma phase in the plasma reformer. Moreover, the nature of the radical species produced in the plasma discharge must be not identical as the species produced at the surface of the catalysts. A further study by emission spectroscopy will be useful to know the composition of the plasma and the nature of radical species.

The main objective of this work was to develop a non-thermal flexible plasma reactor able to work both in auto-thermal and steam reforming conditions and to produce a hydrogen-rich gas at pressure higher than $10^5$ Pa. This work required thus an important technological advance since no plasma reactor has already been developed to work in these conditions. The second step of this work will be to optimize the chemical efficiency of the plasma reactor.

The hydrodynamic feature of the reactor plays an important role on the mixing of the different reactants, the interaction between the plasma and the gas and thus on the efficiency of the process. The main next point will be therefore to improve the geometry of the reactor (volume, size, electrode shape and configuration), the gas flow and the mixing in the reactor for a better interaction between the discharge and the gas. A new plasma reactor with a vortex gas flow will then be developed to optimize the volume treated by the discharge, the mixing between the active species and the heat transfers.

The second main important point will be to optimize the power supply for a better control of the power in the discharge. The chemical efficiency of the plasma reformer can indeed be significantly improved by acting on the electric power delivered by the plasma to the gas since the concentration of

Table 5
Chemical efficiency of several catalytic reformers (ATR: auto-thermal reforming, STR: steam reforming)

| Hydrocarbon | Experimental conditions | | | | | | Products concentration (dry vol.%) | | | | $\eta$ (%) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Chemical reaction | Air ratio | S/C | Fuel power (kW) | Pressure (bar) | Inlet temperature (K) | $H_2$ | CO | $CO_2$ | $CH_4$ | | |
| Methane | ATR | 0.44 | 0.5 | 5 | 1 | ? | 30.5 | 8.9 | 7.1 | 0.2 | 78.4 | [26] |
| Heptane | STR | – | 7 | ? | ? | 843 | 78.8 | 4.6 | 16.5 | 0 | ? | [23] |
| Methane | STR | – | 3–3.5 | 9 | 1.5 | 750–900 | 75.8 | 9 | 12.2 | 3 | 70 | [26] |

the active species directly depends on this power. It will thus be important to increase and control the power delivered in the discharge independently of the operating parameters. The control of the electric current implies to change drastically the secondary electric scheme by replacing the resistance by inductive components.

Finally, we have demonstrated that the operating temperature plays a significant role on the efficiency of the process: increasing the hydrogen yield needs to operate at higher temperature (at 973 K or higher). Several options are then possible: increase the temperature of the feeds, increase the electric power injected in the discharge, or working with a high air ratio. This study will have however to consider the hydrogen yield and reformer efficiency as well as the possible carbon soot production which may pollute the fuel cells in a second step.

## 7. Conclusion

The results presented here correspond to the first development stage of a non-thermal plasma reactor for gasoline reforming.

The objectives of this work were to design a compact plasma reformer for automotive application and to demonstrate the feasibility of producing hydrogen using the non-thermal gliding arc technology in a gaseous phase in auto-thermal and steam reforming conditions at pressure higher than $10^5$ Pa. These objectives have been achieved. The results presented in this paper have confirmed the catalytic effect of the non-thermal gliding discharge and the possibility to produce hydrogen-rich gas from fuel reforming using this technology. A reliable plasma prototype able to work during several hours has been developed. This plasma reformer is very flexible: it is possible to change the geometry of the electrodes, the reaction volume, the inter-electrode gap and to work with one or two gliding arcs in series. It can operate in a large range of operating conditions: auto-thermal or steam reforming conditions. The system allows the use of different feed stocks and is very tolerant to sulphur content and carbon deposit. The important advantages of this technology for the automotive applications are its very short time start-up (few seconds), the large operating range of fuel power (from 10 to 40 kW), its compactness and robustness. The simplicity of the technology and the low cost of the materials are also very attractive for a commercial application.

The current plasma reformer efficiency reaches 12.3% in auto-thermal reforming and 26% in steam reforming for a pressure equal to $2 \times 10^5$ Pa. This efficiency could however be drastically increased by working at higher pressure (2.5 or $3 \times 10^5$ Pa) and especially at higher temperature (1000 K or higher).

A large amount of technological efforts remains to be performed in order to increase the hydrogen yield and improve drastically the chemical efficiency of the plasma reactor. The next step of this work will be thus focused on the following points:

- Improvement of the hydrodynamic features of the plasma reactor.
- Control of the electric power delivered in the plasma discharge.
- Increase of the operating temperature.

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