



# Syngas production from methane oxidation using a non-thermal plasma: Experiments and kinetic modeling

Jocelyn Luche, Olivier Aubry, Ahmed Khacef, Jean-Marie Cormier\*

GREMI-Polytech'Orléans, 14 rue d'Issoudun, B.P. 6744, 45067 Orléans Cedex 2, France

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## ABSTRACT

The laboratory-scale behaviour of a methane–air mixture injected at atmospheric pressure and ambient temperature into a non-thermal plasma (NTP) reactor is investigated experimentally and numerically as a function of CH<sub>4</sub> concentration and mass flow rate. Numerical simulations of the NTP reactor gas phase are performed with a chemical kinetic model used initially for CH<sub>4</sub> oxidation in a perfectly stirred reactor (PSR). The computed H<sub>2</sub>, CO, CO<sub>2</sub> and remaining CH<sub>4</sub> mole fractions are in good agreement with experimental data. Syngas (H<sub>2</sub> and CO) production from CH<sub>4</sub>–air mixture is demonstrated over a large range of fuel flow rates and methane amounts in air. The lowest energy cost of H<sub>2</sub> production is about 45 kWh/kg<sub>(H<sub>2</sub>)</sub> for the highest mass flow rate. Numerical simulation has confirmed that the optimum use of electrical power by the NTP reactor is achieved for high mass flow rates and low inlet CH<sub>4</sub> concentration in air.

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## 1. Introduction

To meet the increasingly stringent environmental regulations on pollution-related problems (nitrogen oxides, greenhouse gases, fine particle matter), several scientific studies have developed alternative and renewable technologies for energy and electricity production. An extensively studied way of improving combustion processes and drastically decreasing noxious emissions is fuel–air conversion into synthetic gas (H<sub>2</sub> + CO), also known as syngas.

Traditionally, syngas production has been achieved by using catalytic reformers [1–6]. However, in addition to its high economic investment cost [7–11], this conventional technology presents several drawbacks. The catalyst device can be poisoned by sulfur or halogen-containing compounds [11–15] and catalyst surface performances can be reduced by solid carbon adsorption or deposition [8–12,16–18]. The treatment or maintenance required to remove the contaminated catalytic equipment can represent a major drawback with respect to current environmental regulations [7–11]. Moreover, catalytic sites need to be activated by heating at high temperature [7–10,12,13,15,16,18,19]. Another problem reported in the literature is the low flow rate of inlet gas injected into catalyst devices [15].

To overcome all these catalyst difficulties, fuel reforming by non-conventional technology such as plasma (both thermal and

non-thermal) technology is being increasingly investigated. Thermal plasma, in which the electron temperature (>10,000 K) is equal to the gas temperature, has been successfully used in fuel–air mixture conversion into syngas to increase internal combustion engine efficiency and to reduce NO<sub>x</sub> emissions [20–22]. While a previous study [22] has shown that comparable H<sub>2</sub> yields can be obtained with thermal and non-thermal plasmas, energy consumption is significantly lower in the case of non-thermal plasma (NTP), in which the electron temperature (>10,000 K) is higher than the gas temperature (300–3000 K) [10,11,19,23–26]. The main role of such a plasma is to provide energy for the production of reactive species (radicals, electron and ions) and to enhance fuel reforming reactions [7–30]. Thus, for approximately thirty years, NTP technologies have been successfully applied to combustion processes to produce H<sub>2</sub> and CO from the reforming of methane or natural gas [7–9,12,16–19,27–30], ethanol [23], propane [9,30], pentane [9], hexane [10] or gasoline [11,13,14,20,21].

The purpose of this work is to evaluate experimentally and numerically the conversion of methane–air mixture into syngas by using a laboratory-scale non-thermal plasma reactor. In the following section, the experimental devices, with parametrical conditions and chemical analyzers are briefly presented. Section 3 describes and discusses the experimental results of the CH<sub>4</sub>/air mixture partial oxidation conditions. In this part, the energy cost of hydrogen production is systematically given as a function of the methane composition in air and mass flow rate. The numerical assumptions chosen to model the species behaviour in NTP reactor are briefly described in Section 4. Numerical mole fractions

\* Corresponding author. Tel.: +33 2 38 49 46 09; fax: +33 2 38 41 71 54.  
E-mail address: [jean-marie.cormier@univ-orleans.fr](mailto:jean-marie.cormier@univ-orleans.fr) (J.-M. Cormier).

### Nomenclature

$[\text{CH}_4]_0$	initial concentration of methane in air (%)
$EC_{\text{H}_2}$	energy cost per kg of $\text{H}_2$ produced ( $\text{kWh}/\text{kg}(\text{H}_2)$ ),
$h_k$	mass enthalpy of the $k$ th species ( $\text{J g}^{-1}$ ),
$h_k^*$	mass enthalpy of the $k$ th species at inlet conditions ( $\text{J g}^{-1}$ ),
$\dot{m}$	mass flow rate ( $\text{g s}^{-1}$ ),
$P_{\text{ch}}$	chemical reaction power exchange (W),
$P_{\text{el}}$	electrical power corresponding to Joule heating of plasma column (W),
$P_{\text{fr}}$	power exchange due to enthalpy and mass flow rate variations (W),
$P_{\text{tc}}$	heat power losses or thermal conduction exchanges (W),
$ Q $	power taking into account heat loss or heat inlet through reactor wall (W),
$\mu_k$	molecular weight of the $k$ th species ( $\text{g mol}^{-1}$ ),
$V$	reaction volume ( $\text{cm}^3$ ),
$W_k$	molar rate of production of the $k$ th species per unit of volume ( $\text{mol cm}^{-3} \text{s}^{-1}$ ),
$Y_k$	mass fraction of the $k$ th species,
$Y_k^*$	mass fraction of the $k$ th species at inlet conditions.

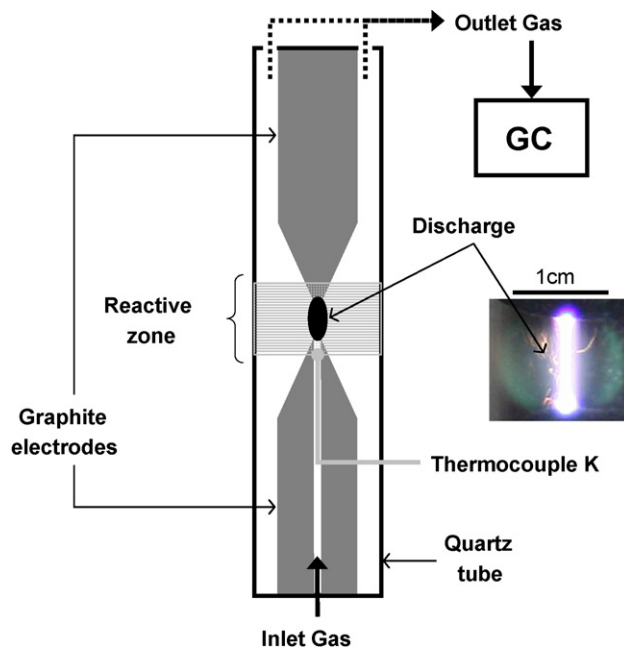


Fig. 1. Schematic representation of the plasma reactor with a photography of the electrical discharge.

and power results are computed by using a chemical kinetic model usually dedicated to methane oxidation in combustion studies. Section 5 presents comparisons between numerical modeling results and experimental measurements considering  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and the remaining  $\text{CH}_4$  mole fractions. The energy efficiency of the NTP system is also discussed by comparing numerical and experimental results.

## 2. Experimental devices

Laboratory-scale experiments were carried out with a  $\text{CH}_4/\text{air}$  mixture injected at atmospheric pressure and room temperature ( $T \sim 295 \text{ K}$ ) into a non-thermal plasma reactor (Fig. 1). The NTP reactor includes a quartz tube (400 mm length and 30 mm inner diameter) containing two electrodes made of graphite. The conical extremities of the two electrodes are placed opposite each other in the central axis of the reactor and with a 10 mm gap. The discharge column resembles a plasma string with a diameter of 2 mm diameter and length of 10 mm (Fig. 1).

Experiments are carried out with initial methane concentrations in air  $[\text{CH}_4]_0$ , ranging from 18 to 40% (volume). The chosen  $[\text{CH}_4]_0$  are higher than the upper explosive limit (16%  $\text{CH}_4$  in air). The upper value of 40% methane in air was chosen in order to avoid significant soot deposition on the reactor wall and to prevent the formation of a soot-bridge between the electrodes, leading to the electrical short-circuit of the system. Moreover, in our experimental conditions, small amounts of solid carbon particles or soot deposits are systematically observed on electrodes, quartz tube and sample pipes. These solid carbon deposits, which do not disrupt the experimental process, explain the deficit in total carbon amounts between the results of exhaust gas and initial methane/air mixture mole fractions.

The  $\text{CH}_4/\text{air}$  mixture is introduced into the reactor through the bottom electrode at a total mass flow rate ranging from 0.004 to  $0.175 \text{ g s}^{-1}$ . Exhaust gas is sampled through holes in the upper part of the reactor and is cooled down in order to eliminate water before chemical analysis. Dry output gas is analyzed and  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$  species are quantified using a gas

phase chromatography analyzer (GC-Varian CP 3800). Two columns (5 Å Molecular Sieve and Hayesep A) are included in the GC analyzer equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID), respectively. These detectors were calibrated with standards of known composition. The maximum relative deviations on mole fractions measured during calibrations are  $\pm 5\%$ .

The mean temperature of the  $\text{CH}_4/\text{air}$  mixture before the plasma discharge is measured by a K-type thermocouple. The maximum deviation on the measured temperature is about  $\pm 20 \text{ K}$ . Fig. 2 shows the variation in this temperature as a function of total mass flow rate. When the mass flow rate increases from 0.004 to  $0.175 \text{ g s}^{-1}$ ,

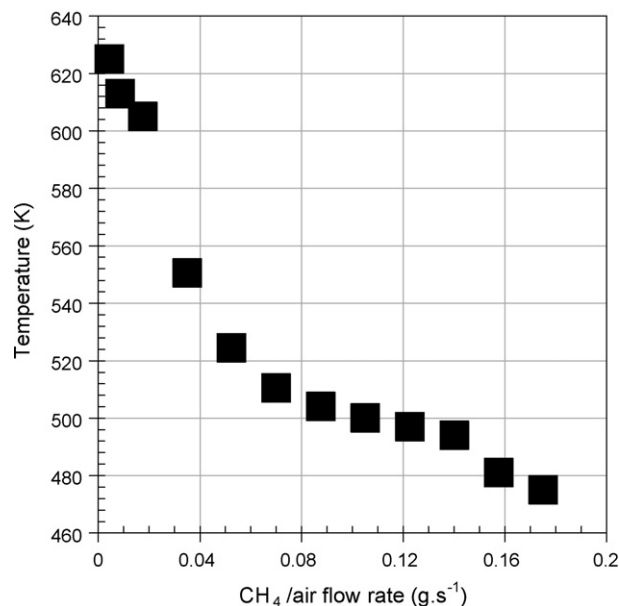


Fig. 2. Gas temperature at the inlet of reactive zone vs.  $\text{CH}_4/\text{air}$  mass flow rate ( $[\text{CH}_4]_0 = 25\%$ ).

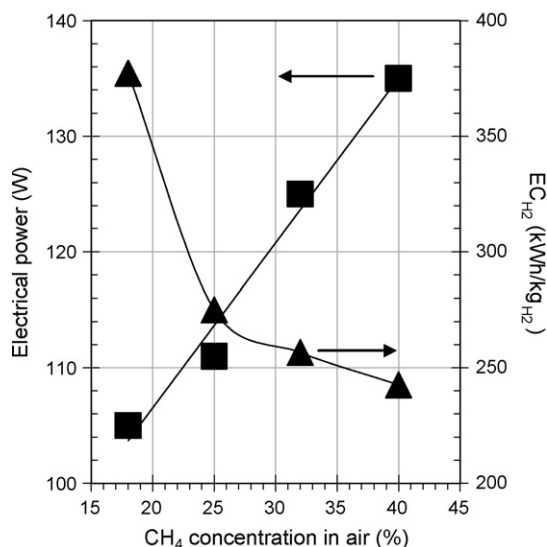


Fig. 3.  $P_{el}$  and  $EC_{H_2}$  vs. initial  $CH_4$  concentration in air (mass flow rate =  $0.004 \text{ g s}^{-1}$ ).

the temperature at the inlet of reactive volume decreases from 630 to 480 K, respectively.

The plasma reactor is powered by a 50 Hz high voltage (15 kV) step-up transformer with leakage flux which produces a sinusoidal current waveform with a constant root mean square value of 155 mA. The non-equilibrium (non-thermal) nature of the plasma created in these conditions has been demonstrated previously [23,30,31]. This plasma is characterized by: (i) a substantial difference between the electron temperature ( $>10,000 \text{ K}$ ) and gas temperature (300–3000 K), (ii) a high electrode voltage drop ( $>100 \text{ V}$ ), and (iii) a low current ( $<200 \text{ mA}$ ). The current and voltage were measured using a TCP202 Tektronix Hall effect probe and a ST500 high voltage differential probe, respectively. Signals from these probes are recorded on a Tektronix TDS 460A digital oscilloscope and processed on a PC. The mean electrical discharge power is computed from voltage–current waveforms ( $P_{el} = \frac{1}{T} \int u(t) \cdot i(t) \cdot dt$ ) and averaged over a large number of discharges. Results are shown as a function of methane concentration and mass flow rate in the next section (Figs. 3 and 6, respectively). The mean power values are in the range 100–160 W depending on experimental conditions.

### 3. Experimental results and discussion

Dry outlet species analyses were carried out for the following experimental conditions:

- Inlet  $CH_4$  concentration ranged from 18 to 40% (volume) in air for a total mass flow rate kept constant at about  $0.004 \text{ g s}^{-1}$ ,
- 25%  $CH_4$  in air for a mass flow rate ranged from 0.004 to  $0.175 \text{ g s}^{-1}$ .

#### 3.1. $CH_4$ concentration effect on outlet gas concentrations

Exhaust gas mole fractions (symbols) are shown in Fig. 4 as a function of the initial concentration of  $CH_4$  in Air. As  $[CH_4]_0$  increases from 18 to 40%, the  $H_2$  mole fraction increases from 0.19 to 0.39 and the  $CH_4$  mole fraction from 0.01 to 0.06, respectively. The CO mole fraction increases slightly from 0.13 to 0.15 while the  $CO_2$  mole fraction decreases from 0.03 to 0.00. In these experiments,  $C_3$  and  $C_4$  hydrocarbon concentrations measured on a GC analyzer are below 20 ppm and can be considered as negligible compared to  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$  concentrations. Indeed,  $C_2$  species mole

fractions increase with increasing  $[CH_4]_0$  and always stay below 0.02. These results suggest that initial  $CH_4$  is mainly consumed to produce syngas ( $H_2 + CO$ ) by partial oxidation (POX) reaction ( $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ ).

Fig. 3 gives electrical power ( $P_{el}$ ) and energy cost of  $H_2$  production ( $EC_{H_2}$ ) as a function of initial  $CH_4$  concentration in air.  $EC_{H_2}$  is computed from the following expression:  $EC_{H_2} = P_{el}/(3600 \cdot D_{H_2})$ , where  $D_{H_2}$  is the mass flow rate of dry  $H_2$  produced and  $P_{el}$  the reactor discharge power. In the experimental device, the mass flow rate of exhaust gas is 1.13 ( $\pm 0.03$ ) times the initial mass flow rate.  $P_{el}$  increases from 105 to 135 W and  $EC_{H_2}$  decreases from 380 to 240 kWh/kg( $H_2$ ) for an increase of  $[CH_4]_0$  from 18 to 40%, respectively. These results show that for the highest  $CH_4$  amount in air,  $H_2$  mole fraction and  $P_{el}$  are maximum (0.4 and 130 W, respectively) corresponding to the lowest  $EC_{H_2}$  value ( $\sim 240 \text{ kWh/kg}(H_2)$ ).

#### 3.2. $CH_4$ /air mixture flow rate effect on outlet gas concentrations

Fig. 5 shows outlet gas mole fractions (symbols) as a function of  $CH_4$ /air mass flow rate. It can be seen that the  $H_2$  mole fraction decreases from 0.29 to 0.05 and the CO mole fraction from 0.17 to 0.03. Furthermore, the remaining  $CH_4$  mole fraction increases from 0.02 to 0.20, while the  $CO_2$  and  $C_2$  mole fractions stay in all cases below 0.01. No significant amount of species heavier than  $C_2$ -hydrocarbons was observed in these experiments.

Results suggest that  $CH_4$  conversion by POX reaction into syngas is enhanced by a low  $CH_4$ /air mass flow rate. In these experimental conditions, the residence time in the plasma reactor increases, promoting the production of active species and thus enhancing the methane partial oxidation into syngas. The discharge occurs as a column between the conical extremities of the two electrodes in the axis of the plasma reactor (Fig. 1). When the mass flow rate increases, the velocity of the  $CH_4$ /air mixture exiting the bottom electrode increases, causing an increase in plasma discharge length. At high mass flow rate, the plasma discharge moves away from the axis of the reactor towards the quartz tube wall where the gap is much higher than 10 mm. In that case, only part of the  $CH_4$ /air mixture is treated by the discharge, leading to the low production of  $H_2$  by POX reaction.

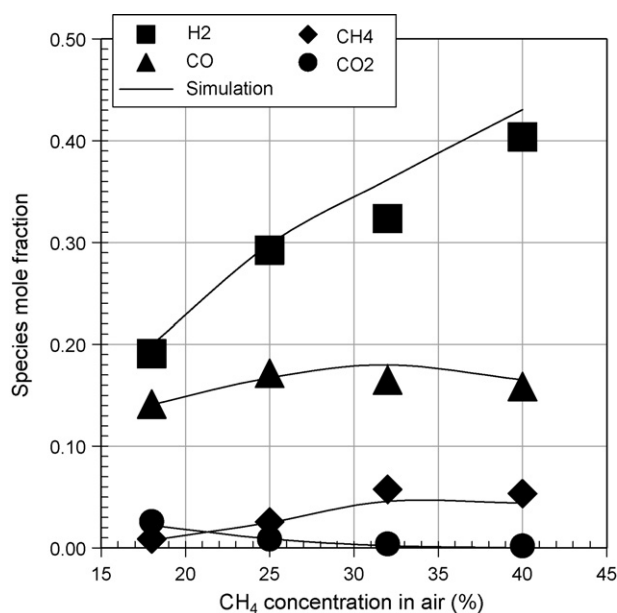


Fig. 4. Experimental (symbols) and numerical (lines)  $H_2$ , CO,  $CO_2$  and  $CH_4$  mole fractions vs. initial  $CH_4$  concentration in air (mass flow rate =  $0.004 \text{ g s}^{-1}$ ).

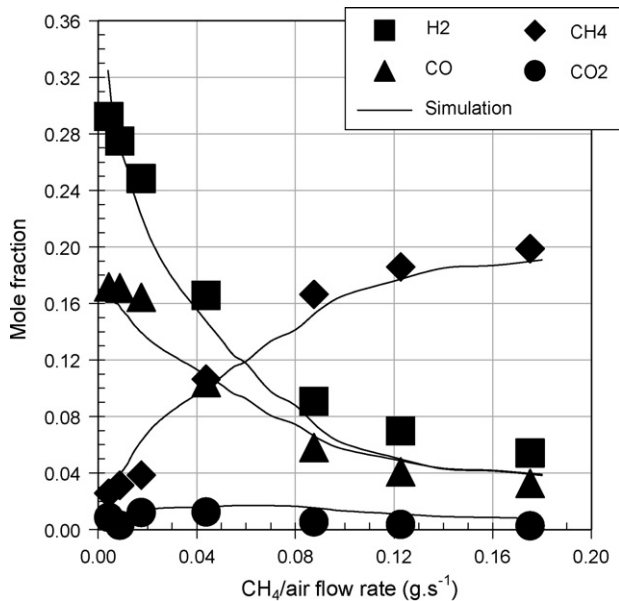


Fig. 5. Experimental (symbols) and numerical (lines) H<sub>2</sub>, CO, CO<sub>2</sub> and remaining CH<sub>4</sub> mole fractions vs. CH<sub>4</sub>/air mass flow rate ([CH<sub>4</sub>]<sub>0</sub> = 25%).

Fig. 6 shows electrical power and energy cost of H<sub>2</sub> production as a function of mass flow rate.  $P_{el}$  increases from 110 to 155 W and  $EC_{H_2}$  decreases from 275 to 50 kWh/kg<sub>(H<sub>2</sub>)</sub> for a mass flow rate increasing from 0.004 to 0.175 g s<sup>-1</sup>, respectively.

For the highest total mass flow rate (0.175 g s<sup>-1</sup>) studied, the H<sub>2</sub> mole fraction is minimum and  $P_{el}$  is maximum (0.05 and 155 W, respectively) corresponding to the lowest  $EC_{H_2}$  value (~45 kWh/kg<sub>(H<sub>2</sub>)</sub>). From these results, it appears that the best energy costs are achieved for the highest mass flow rate studied and are in quite good agreement with those reported in the literature: around 1 kWh/kg<sub>(H<sub>2</sub>)</sub> for plasma technology assisted by catalysis [32], from 1 to 139 kWh/kg<sub>(H<sub>2</sub>)</sub> for gliding arc technology [29,30,33], up to 30 kWh/kg<sub>(H<sub>2</sub>)</sub> for corona discharge technology [34], from 300 to 4000 kWh/kg<sub>(H<sub>2</sub>)</sub> for dielectric barrier discharge technology [35], and from 17 to 1000 kWh/kg<sub>(H<sub>2</sub>)</sub> for conventional technology (autothermal, O<sub>2</sub>/air-fired or steam reformer) or electrolytic processes [36–39].

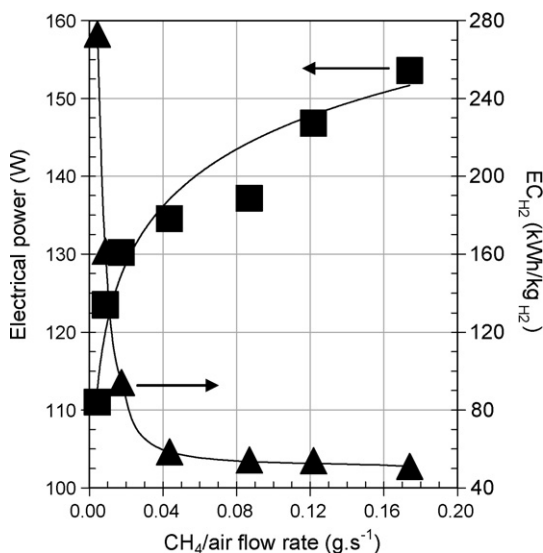


Fig. 6.  $P_{el}$  and  $EC_{H_2}$  vs. mass flow rate ([CH<sub>4</sub>]<sub>0</sub> = 25%).

## 4. Simulation

### 4.1. Reactor model

Kinetic modeling is a useful tool to study gas phase processes and to gain insight into the chemical mechanisms inside an experimental bulk gas phase. Non-thermal plasma provides energy for active species generation: electrons, ions and free radicals which are involved in the chemical reactions induced. However, modeling with plasma mechanisms describing in detail both chemical kinetics and fluid dynamics is not easily available today. To simulate the experimental methane reforming process by NTP, numerical computations were performed with the following assumptions [15,24,40,41]:

- Thermal decomposition is assumed to be negligible at the inlet of the plasma reactor for initial experimental conditions (295–630 K).
- The discharge effect is considered as an additional energy source to the chemical processes inside the reactor.
- The methane reforming by NTP is described only by the radical behaviour and takes place mainly in the reactive volume ( $V \approx 7.1 \text{ cm}^3$ ). Modeling is performed only with a kinetic scheme of the methane oxidation chemistry process in gas phase without the inclusion of specific plasma processes (post-discharge kinetics).
- Radical production is proportional to the related bulk gas composition.
- Radicals and reactants are well mixed and uniformly distributed (i.e. 0-D model) within the reactive volume which is assumed to be equivalent to a perfectly stirred reactor (PSR).

Chemical transformation computations, performed with the PSR code [42] from the CHEMKIN-II package [43] and methane reforming chemical kinetics by a non-thermal plasma, are conducted by using the Konnov methane oxidation mechanism [44,45]. Input parameters of the model are:

- constant flow rate (0.004 g s<sup>-1</sup>) for [CH<sub>4</sub>]<sub>0</sub> ranged from 18 to 40%,
- [CH<sub>4</sub>]<sub>0</sub> = 25% at flow rate in the range 0.004–0.175 g/s,
- atmospheric pressure,
- gas temperature at the inlet of the plasma discharge as a function of mass flow rate (480–630 K, see Fig. 2),
- each experimental mole fraction is simulated by numerical fitting of an adjusted negative value of  $Q$  (heat inlet through reactor walls corresponds to  $Q < 0$ ) taking into account discharge electrical power, mass flow rate and initial CH<sub>4</sub> concentration.

### 4.2. Energy balance: experimental and modeling

In the steady state case at constant temperature, the energy conservation equation for a PSR can be written:

$$Q = \dot{m} \cdot \sum_{k=1}^N Y_k^* \cdot (h_k^* - h_k) - V \cdot \sum_{k=1}^N h_k \cdot W_k \cdot \mu_k \quad (1)$$

The first and second terms of Eq. (1) represent the power exchange due to mass enthalpy variations and mass flow rate (Eq. (2)) and the power exchange due to chemical reactions (Eq. (3)), respectively.

$$P_{fr} = -\dot{m} \cdot \sum_{k=1}^N Y_k^* \cdot (h_k^* - h_k) \quad (2)$$



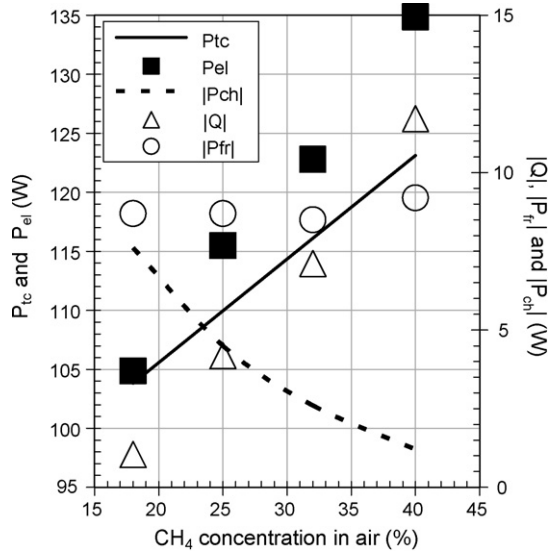


Fig. 7.  $P_{tc}$ ,  $P_{el}$ ,  $|Q|$ ,  $|P_{fr}|$ ,  $|P_{ch}|$  values vs.  $CH_4$  amount (mass flow rate =  $0.004 \text{ g s}^{-1}$ ).

$$P_{ch} = -V \cdot \sum_{k=1}^N h_k \cdot W_k \cdot \mu_k \quad (3)$$

The energy balance is the sum of various contributions:

- electrical power corresponding to Joule heating of the plasma column ( $P_{el}$ ),
- heat power losses or thermal conduction exchanges at high flow rates ( $P_{tc}$ ),
- power exchange due to flow rate with enthalpy variations per unit of mass ( $P_{fr}$ ),
- power exchange due to chemical reactions ( $P_{ch}$ ).

By neglecting radiation losses in the case of electrical discharge, the energy balance can be written by the following expression:

$$P_{el} - P_{tc} - P_{fr} + P_{ch} = 0 \quad (4)$$

From Eqs. (1)–(4),  $Q$  can be written as follows:

$$Q = P_{tc} - P_{el} \quad (5)$$

### 5. Numerical results and discussion

#### 5.1. $CH_4$ concentration effect on exhaust gas concentration

The calculated outlet species mole fractions obtained by using the above PSR model and the heat exchange power ( $Q$ ) as fitting parameter are compared to experimental data. Taking into account the calculated species' concentrations and  $Q$  value, both  $P_{ch}$  and  $P_{fr}$  can also be calculated. Experimental (symbols) and numerical (line) species mole fractions are shown as a function of initial  $CH_4$  concentration in air in Fig. 4. For  $[CH_4]_0$  in the range 18–40%, good agreement (within 5–10%) is observed between the computed  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$  mole fractions and experiments.

In Fig. 7, the computed values of  $|Q|$ ,  $|P_{ch}|$ ,  $|P_{fr}|$  and  $P_{tc}$  and the experimental values of  $P_{el}$  are plotted as a function of  $CH_4$  amount. When  $[CH_4]_0$  increases from 18 to 40%, the values of heat exchanges  $|Q|$  increase from 1 to 12 W. This increase in  $|Q|$  value (linked to the initial increase in  $CH_4$  amount) leads to an increase in power exchange values ( $P_{tc}$  from 105 to 125 W, or  $|P_{fr}|$  from 8 to 9 W).  $|P_{ch}|$  decreases from 8 to 1 W and  $P_{el}$  increases from 105 to 135 W. From Fig. 7, it can be seen that  $|P_{ch}|$  represents only 1–8% of  $P_{el}$ . Thus,

only a small part of the electrical energy supplied is involved in partial oxidation of methane. So, when the  $CH_4$  amount increases, a major part of the discharge energy, corresponding to  $P_{el}$ , is lost by heat transfer and thermal conduction exchanges,  $P_{tc}$  and  $|P_{fr}|$ , respectively. These results show that the highest power efficiency to convert methane (higher  $|P_{ch}|$  and lower  $P_{tc}$  or  $|P_{fr}|$  values) into syngas is observed for low  $[CH_4]_0$ .

In the whole range of  $CH_4$  amount, the assumptions chosen ( $|Q|$  in the range 1–12 W and PSR configuration) to simulate  $CH_4$ /air treatment by a non-thermal plasma are fully satisfactory. The  $CH_4$  oxidation kinetic model of Konnov can describe  $H_2$ ,  $CO$ ,  $CO_2$  and  $CH_4$  species mole fractions with a relatively good precision (within 5–10%). Thus, only a small part of the electrical energy supplied contributes to the chemical reaction and most of this electrical energy is involved in thermal losses.

#### 5.2. Mass flow rate effect at outlet gas concentration

Comparison between experimental (symbols) and numerical (line) data as a function of  $CH_4$ /air mass flow rate is shown in Fig. 5 at a given  $[CH_4]_0$  (25%). Numerical mole fractions are in good agreement ( $\pm 5\%$ ) with experimental data for a mass flow rate below  $0.08 \text{ g s}^{-1}$  and a relative difference in the range 5–20% is observed for a mass flow rate equal to or higher than  $0.08 \text{ g s}^{-1}$ .

The computed values of  $|Q|$ ,  $|P_{ch}|$ ,  $|P_{fr}|$  and  $P_{tc}$  and the experimental values of  $P_{el}$  as a function of  $CH_4$ /air mass flow rate are plotted in Fig. 8. A linear variation of  $P_{fr}$  (10–270 W) is observed in the full range of mass flow rate. Fig. 8 shows two domains for  $|Q|$  variations: a first one with a constant variation of  $|Q|$  (value around 10 W) and a second one with a linear increase in  $|Q|$  from 10 to 130 W. These fitted values of  $|Q|$  are linked to two experimental device domains of mass flow rate:

- up to  $0.08 \text{ g s}^{-1}$ , with significant thermal conduction effects or power losses ( $P_{tc}$ ) ranging from 100 to 120 W, corresponding to a significant variation in  $|P_{ch}|$  which increases from 5 to 100 W,
- beyond  $0.08 \text{ g s}^{-1}$ , with a better use of electrical power due to an effect on  $P_{tc}$  value decreasing from 120 to 20 W, corresponding to a slight variation in  $|P_{ch}|$  which increases less significantly (from 100 to 120 W) than previously.

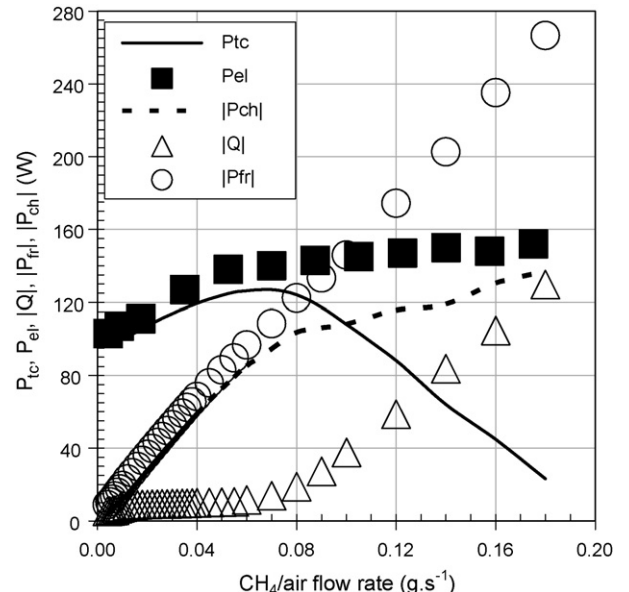


Fig. 8.  $P_{tc}$ ,  $P_{el}$ ,  $|Q|$ ,  $|P_{fr}|$ ,  $|P_{ch}|$  values vs.  $CH_4$ /Air mass flow rate ( $[CH_4]_0 = 25\%$ ).

For low mass flow rates, the mean plasma discharge power,  $P_{el}$ , increases from 100 to 150 W. For a high flow rate,  $P_{el}$  is of the same order of magnitude as the chemical power, and losses by thermal conduction are reduced in comparison with data obtained at low flow rates.

At a low mass flow rate, the assumptions chosen ( $|Q|$  in the range 5–20 W and a perfectly stirred reactor configuration) to simulate  $\text{CH}_4/\text{air}$  treatment by NTP are fully satisfactory. Indeed, the agreement between experimental and numerical data is within 5–10%. As seen previously, only a small part of the electrical energy supplied is involved in chemical reaction (low  $|P_{ch}|$  value) due to high heat transfer and thermal conduction exchanges,  $P_{tc}$  and  $|P_{fr}|$ , respectively. Conversely, for a high mass flow rate (with  $|Q|$  in the range 20–130 W), the results are less satisfactory, though still acceptable (agreement within 5–20% between experimental and numerical results). This slight difference could be explained by a non-uniform species distribution within the reaction zone volume due to plasma instabilities and by a small  $\text{CH}_4$  conversion rate due to a low residence time. The relative depletion of thermal losses in comparison with the electrical energy supplied to the plasma leads to a better energy efficiency of the device to reform the initial mixture (higher  $|P_{ch}|$  value than previously).

## 6. Conclusion

Experimental investigations of a methane–air mixture injected at atmospheric pressure and ambient temperature in a laboratory-scale non-thermal plasma reactor, as well as the chemical analysis of the main gas products ( $\text{H}_2$ , CO,  $\text{CO}_2$  and unburned  $\text{CH}_4$ ) have been carried out. Maximum  $\text{H}_2$  and CO mole fractions in exhaust gas are obtained at a high methane concentration in air (*i.e.* 40%) and low  $\text{CH}_4/\text{air}$  mixture flow rate (*i.e.*  $0.004 \text{ g s}^{-1}$ ). The experimental mean power supplied to the electrical discharge is measured in the range 100–160 W as a function of mass flow rate and  $\text{CH}_4$  amount in air. Furthermore, the energy cost can be computed from the mean electrical power and the hydrogen mass flow rate. The best energy cost of  $\text{H}_2$  production ( $\sim 45 \text{ kWh/kg}_{(\text{H}_2)}$ ) is observed for the highest  $\text{CH}_4/\text{air}$  mixture mass flow rate.

A kinetic approach to  $\text{CH}_4$  reforming by a non-thermal plasma has also been performed using Konnov's oxidation model, initially developed for combustion studies, with assumptions about initial conditions: well-stirred species, gas phase reaction (without specific plasma processes), 0-D model and plasma energy input. Numerical results obtained without any adjustments of the kinetic reactions fit the experimental data rather well, as in all cases, the agreement is within 5–10%. Simulation and experimental data show two main results:

- High  $\text{CH}_4$  conversion and maximum  $\text{H}_2$  production are obtained at low flow rate and high initial concentration of methane in air. In these cases, most of the electrical energy supplied to the plasma is lost by thermal effect and not involved in the chemical reaction, entailing a high energy cost to produce  $\text{H}_2$ .
- A low energy cost of  $\text{H}_2$  production can be obtained at high flow rates and low initial concentration of methane in air, which decreases losses and enables a better use of electrical power by the chemical reactions.

This study has demonstrated that PSR is a powerful tool for the simulation of gas phase behaviour in methane reforming by a NTP reactor. However, further studies are needed in applying PSR in other experimental conditions, initial fuel or plasma reactors. The technical improvement of such a laboratory-scale reactor needs to be performed with a view to industrial applications: this can be

done by considering previous experimental results obtained with gliding discharges [14,15]. Further experiments (*e.g.* in situ spectroscopic diagnostics) can be performed with this NTP reactor to improve the chemical understanding of active species behaviour in the discharge.

## References

- [1] F. Auprêtre, C. Descorme, D. Duprez, Bio-ethanol catalytic steam reforming over supported metal catalysts, *Catal. Commun.* 3 (2002) 263–267.
- [2] G.A. Deluga, J.R. Salge, L.D. Schmidt, X.E. Verykios, Renewable hydrogen from ethanol by autothermal reforming, *Science* 303 (2004) 993–997.
- [3] J. Llorca, N. Homs, J. Sales, P. Ramirez de la Piscina, Ramirez de la Piscina, efficient production of hydrogen over supported cobalt catalysts from ethanol steam reforming, *J. Catal.* 209 (2002) 306–317.
- [4] J.P. Breen, R. Burch, H.M. Coleman, Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications, *Appl. Catal. B: Environ.* 39 (2002) 65–74.
- [5] F.J. Marino, E.G. Cerrella, S. Duhalde, M. Jobbagy, M.A. Laborde, Hydrogen from steam reforming of ethanol. Characterization and performance of copper-nickel supported catalysts, *Int. J. Hyd. Energy* 23 (12) (1998) 1095–1101.
- [6] E.Y. Garcia, M.A. Laborde, Hydrogen production by the steam reforming of ethanol: thermodynamic analysis, *Int. J. Hyd. Energy* 16 (5) (1991) 307–312.
- [7] O. Mutaf-Yardimci, A.V. Saveliev, A.A. Fridman, L.A. Kennedy, Employing plasma as catalyst in hydrogen production, *Int. J. Hyd. Energy* 23 (12) (1998) 1109–1111.
- [8] A. Huang, G. Xia, J. Wang, S.L. Suib, Y. Hayashi, H. Matsumoto,  $\text{CO}_2$  reforming of  $\text{CH}_4$  by atmospheric pressure ac discharge plasmas, *J. Catal.* 189 (2000) 349–359.
- [9] S. Futamura, H. Kabashima, G. Annadurai, Roles of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as oxidants in the plasma reforming of aliphatic hydrocarbons, *Catal. Today* 115 (2006) 211–216.
- [10] H. Sekiguchi, Y. Mori, Steam plasma reforming using microwave discharge, *Thin Solid Films* 435 (1/2) (2003) 44–48.
- [11] T. Paulmier, L. Fulcheri, Use of non-thermal plasma for hydrocarbon reforming, *Chem. Eng. J.* 106 (2005) 59–71.
- [12] A. Czernichowski, GlidArc assisted preparation of the synthesis gas from natural and waste hydrocarbons gases, oil & gas science and technology, *Rev. IFP* 56 (2) (2001) 181–198.
- [13] M.G. Sobacchi, A.V. Saveliev, A.A. Fridman, L.A. Kennedy, S. Ahmed, T. Krause, Experimental assessment of a combined plasma/catalytic system for hydrogen production via partial oxidation of hydrocarbon fuels, *Int. J. Hyd. Energy* 27 (6) (2002) 635–642.
- [14] J.D. Rollier, J. Gonzalez-Aguilar, G. Petitpas, A. Darmon, L. Fulcheri, R. Metkemeijer, Experimental study on gasoline reforming assisted by nonthermal arc discharge, *Energy Fuels* 22 (2008) 556–560.
- [15] A. Indarto, J.W. Choi, H. Lee, H.K. Song, Kinetic modeling of plasma methane conversion using gliding arc, *J. Nat. Gas Chem.* 14 (2005) 13–21.
- [16] L.M. Zhou, B. Xue, U. Kogelschatz, B. Eliasson, Nonequilibrium plasma reforming of greenhouse gases to synthesis gas, *Energy Fuels* 12 (1998) 1191–1199.
- [17] H.D. Gesser, N.R. Hunter, D. Probawono, The  $\text{CO}_2$  reforming of natural gas in a silent discharge reactor, *Plasma Chem. Plasma Process.* 18 (2) (1998) 241–245.
- [18] K. Supat, A. Kruapong, S. Chavadej, L.L. Lobban, R.G. Mallinson, Synthesis gas production from partial oxidation of methane with air in AC electric gas discharge, *Energy Fuels* 17 (2003) 474–481.
- [19] J.M. Cormier, I. Rusu, Syngas production via methane steam reforming with oxygen: plasma reactors versus chemical reactors, *J. Phys. D: Appl. Phys.* 34 (2001) 2798–2803.
- [20] L. Bromberg, D.R. Cohn, A. Rabinovich, J.E. Surma, J. Virden, Compact plasmatron-assisted hydrogen generation technology for vehicular applications, *Int. J. Hyd. Energy* 24 (1999) 341–350.
- [21] L. Bromberg, D.R. Cohn, A. Rabinovich, J. Heywood, Emissions reductions using hydrogen from plasmatron fuel converters, *Int. J. Hyd. Energy* 26 (2001) 1115–1121.
- [22] G. Petitpas, J.D. Rollier, A. Darmon, J. Gonzalez-Aguilar, R. Metkemeijer, L. Fulcheri, A comparative study of non-thermal plasma assisted reforming technologies, *Int. J. Hyd. Energy* 32 (2007) 2848–2867.
- [23] O. Aubry, C. Met, A. Khacef, J.M. Cormier, On the use of a non-thermal plasma reactor for ethanol steam reforming, *Chem. Eng. J.* 106 (2005) 241–247.
- [24] M.S. Benilov, G.V. Naidis, Modeling of hydrogen-rich gas production by plasma reforming of hydrocarbon fuels, *Int. J. Hyd. Energy* 31 (2006) 769–774.
- [25] S. Kado, K. Urasaki, Y. Sekine, K. Fujimoto, Direct conversion of methane to acetylene or syngas at room temperature using non-equilibrium pulsed discharge, *Fuel* 82 (2003) 1377–1385.
- [26] Y.P. Zhang, Y. Li, Y. Wang, C.J. Liu, B. Eliasson, Plasma methane conversion in the presence of carbon dioxide using dielectric-barrier discharges, *Fuel Process. Technol.* 83 (2003) 101–109.
- [27] C.J. Liu, B. Xue, B. Eliasson, F. He, Y. Li, G.H. Xu, Methane conversion to higher hydrocarbons in the presence of carbon dioxide using dielectric-barrier discharge plasmas, *Plasma Chem. Plasma Process.* 21 (2001) 301–310.

- [28] I. Rusu, J.M. Cormier, On a possible mechanism of the methane steam reforming in a gliding arc reactor, *Chem. Eng. J.* 91 (2003) 23–31.
- [29] E. El Ahmar, C. Met, O. Aubry, A. Khacef, J.M. Cormier, Hydrogen enrichment of a methane–air mixture by atmospheric pressure plasma for vehicle applications, *Chem. Eng. J.* 116 (2006) 13–18.
- [30] F. Ouni, Production d'hydrogène et valorisation des alcanes par plasma non thermique, PhD Thesis, Université d'Orléans, GREMI, 2006.
- [31] H. Nassar, S. Pellerin, K. Musiol, O. Martinie, N Pellerin and J-M Cormier,  $N^+_{2}/N_2$  ratio and temperature measurements based on the first negative  $N^+_{2}$  and second positive  $N_2$  overlapped molecular emission spectra, *J. Phys. D: Appl. Phys.* 37 (2004) 1904–1916.
- [32] Y. Chao, C.T. Huang, H.M. Lee, M.B. Chang, Hydrogen production via partial oxidation of methane with plasma-assisted catalysis, *Int. J. Hyd. Energy* 33 (2) (2008) 664–671.
- [33] D.H. Lee, K.T. Kim, M.S. Cha, Y.H. Song, Optimization scheme of a rotating gliding arc reactor for partial oxidation of methane, in: *Proceedings of the Combustion Institute*, vol. 31, 2007, pp. 3343–3351.
- [34] G.B. Zhao, S. John, J.J. Zhang, L. Wang, S. Muknahallipatna, J.C. Hamann, J.F. Ackerman, M.D. Argyle, O.A. Plum, Methane conversion in pulsed corona discharge reactors, *Chem. Eng. J.* 125 (2006) 67–79.
- [35] B. Sarmiento, J.J. Brey, I.G. Viera, A.R. Gonzalez-Elipe, J. Cotrino, V.J. Rico, Hydrogen production by reforming of hydrocarbons and alcohols in a dielectric barrier discharge, *J. Power Sources* 169 (2007) 140–143.
- [36] N. Muradov, F. Smith, A. T-Raissi, Hydrogen production by catalytic processing of renewable methane-rich gases, *Int. J. Hyd. Energy* 33 (2008) 2023–2035.
- [37] C.E. Thomas, I.F. Kuhn Jr., B.D. James, F.D. Lomax Jr., G.N. Baum, Affordable hydrogen supply pathways for fuel cell vehicles, *Int. J. Hyd. Energy* 23 (6) (1998) 507–516.
- [38] C.E. Thomas, B.D. James, F.D. Lomax Jr., I.F. Kuhn Jr., Fuel options for the fuel cell vehicle: hydrogen, methanol or gasoline? *Int. J. Hyd. Energy* 25 (2000) 551–567.
- [39] M. Jasinski, M. Dors, J. Mizeraczyk, Production of hydrogen via methane reforming using atmospheric pressure microwave plasma, *J. Power Sources* 181 (2008) 41–45.
- [40] S.A. Nair, T. Nozaki, K. Okazaki, Methane oxidative conversion pathways in a dielectric barrier discharge reactor—investigation of gas phase mechanism, *Chem. Eng. J.* 132 (2007) 85–95.
- [41] A. Indarto, J.-W. Choi, H. Lee, H.K. Song, Methane conversion using dielectric barrier discharge: comparison with thermal process and catalyst effects, *J. Nat. Gas Chem.* 15 (2006) 87–92.
- [42] P. Glarborg, R.J. Kee, J.F. Grcar, J.A. Miller, PSR: A FORTRAN program for modeling well-stirred reactors, Sandia Report SAND86-8209, 1986.
- [43] R.J. Kee, F.M. Rupley, J.A. Miller, CHEMKIN-II: A fortran chemical kinetics package for the analysis of gas-phase chemical kinetics, Sandia Report SAND89-8009, 1989.
- [44] A.A. Konnov, Detailed reaction mechanism for small hydrocarbons combustion, Release 0.5 <http://homepages.vub.ac.be/~akonnov/>, 2000 (accessed August 2008).
- [45] A.A. Konnov, Development and validation of a detailed reaction mechanism for the combustion of small hydrocarbons, *Proceedings of the Combustion Institute* 28 (2000) 317.