Burst and nanopulsed discharges for non-oxidative methane reforming : a comparison

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Abstract: Hydrogen production relies heavily on hydrocarbons and CO_2-intensive processes. Cold plasma conversion of methane to hydrogen and hydrocarbons/solid carbon is an alternative route for a cleaner production. The aim of our work is to study the energy distribution in time through pulsing of a dielectric barrier discharge. Impact of the energy by pulse on methane conversion and products selectivity is described.

Keywords: DBD, nanopulse, burst, methane, hydrogen

1. Introduction

In the effort of decarbonating the current energy market, hydrogen emerges as an interesting candidate to act both as a fuel and an energy storage media. However, current production means are relying on fossil fuels and emit greenhouse gases. On the other hand, water splitting is associated with a high ernergetic cost.[1] Methane decomposition to hydrogen, higher hydrocarbons and solid carbon is a promissive process, allowing for both low theoretical energetic cost (standard enthalpy at 298 K of Equation 1 : 37,4 kJ/ mol_{H_2} for the decomposition of methane, against 285,83 kJ/mol_{H_2} for water splitting) and avoiding greenhouse gases emissions.

$$CH_4\ (g) \rightarrow\ 2H_2\ (g) + C\ (s) \qquad (1)$$

Cold plasma processes, among which dielectric barrier discharges (DBDs), are the focus of many studies to probe their potential for this application.[2] Control of the energy in the discharge, and how it is distributed through time, is an essential parameter to optimize DBDs efficiency. In this work, we look into the effect of pulsing a discharge, ie applying a constant average power but alternating ON and OFF times of the plasma in order to modify the instantaneous power dissipated in the discharge. Two pulsing modes are compared, the so-called "burst" mode, consisting of few periods of AC current and voltage, and the nanopulsed mode, where a DC voltage is applied for approximately 250 ns. These techniques, along with a cylindrical DBD reactor, allow for an easy and ON/OFF process. DBDs are generally associated with low energy efficiency for this application, because a significant amount of the power is transferred in vibrational energy, which is then lost as heat through collisions. Using a nanopulsed discharge has been pointed has a possible improvement for energy efficiency, since it limits heating of the gas.[3] Burst mode has also shown better results than traditional AC in other applications.[4]

2. Experimental

The DBD reactor used for this study is represented in Fig 1, and is similar to what has been described in previous work from our group.[5] It consists of two concentric cylindrical electrodes, a copper rod (radius : 22 mm) in the center and a stainless steel mesh on the outside. The stainless steel mesh is wrapped around the dielectric over 10 cm (the length of the discharge), in this case a borosilicate tube (inter and outer radii : 26 and 30 mm). 100 sccm of methane is flown through the reactor for all experiments. High voltage is applied with two different generators. An AFS G10S-V for experiments in burst mode, and a Eagle Harbor Technologies NSP for nanopulsed discharges. Gaseous products are characterized with a quadrupolar mass spectrometer from Hiden.

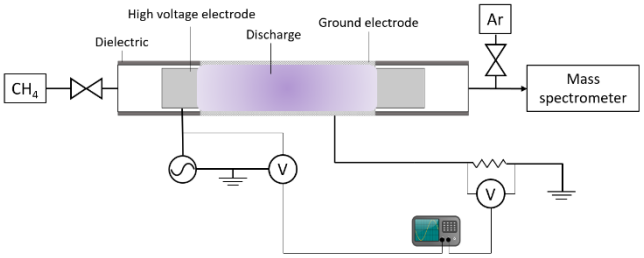

Fig. 1. Schematic of the DBD reactor

A reference flow of 100 sccm of argon is added to the reaction products before entering the mass spectrometer for detection of variations of the total flow. Voltage is measured with a P6015A probe (Tektronix). Current is measured with a voltage probe placed on an additional resistor in serie with our system. Voltage and current are recorded on a DPO3032 oscilloscope (Tektronix).

The window of studied power was limited by experimental constraints. A minimal power for total ignition of the discharge was necessitated, and higher powers were limited to avoid arcing and damaging the dielectric. The distribution of the power is either described by the Pulse Repetition Frequency (PRF) for a nanopulsed discharge, or either by the Duty Cycle (DC) for the burst mode. The duty cycle represents the part of time during which the high voltage is applied. Duty cycle is given by Equation 1, where T refers to the time (in seconds) when the high voltage is applied (T_{ON}) or not (T_{OFF}) :

$$DC\ (\%) = \frac{T_{ON}}{T_{OFF} + T_{ON}} \qquad (2)$$

3. Results

An average power of 18 W was applied during both nanopulsed and burst experiments. DC of 20, 25 and 33% and PRF of 3, 4,5 and 6 kHz were investigated. These powers correspond to different instantaneous powers, described in Table 1. The shape of the DC and nanopulses are illustrated by Figure 2.

Table 1. Power in function of the parameters

Instantaneous power (W)					
Duty cycle			Pulse repetition frequency		
20 %	25 %	33 %	3 kHz	4.5 kHz	6 kHz
95 (± 5)	73 (± 2)	53 (± 3)	5890 (± 20)	4010 (± 55)	3050 (± 70)

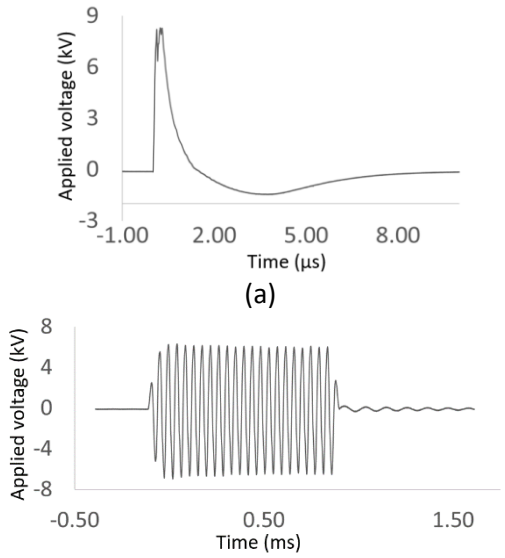

Fig. 2. Shape of the applied voltage for (a) a nanopulse (b) a burst in a duty cycle

For these conditions, no significant variations in conversion or selectivity was observed inside of each mode. However, the conversion was greater in the nanopulsed mode, as illustrated in Figure 3.

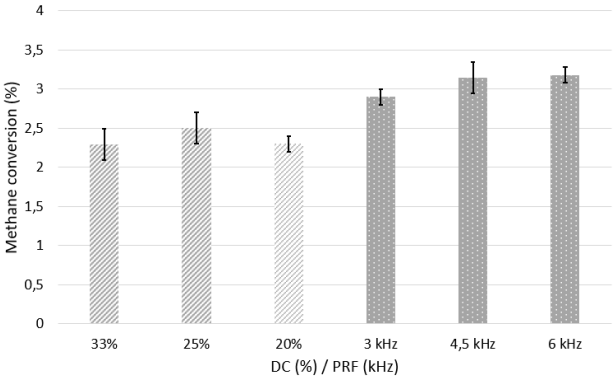

Fig. 3. Comparison of the conversion of methane in burst and nanopulsed mode

This trend seems to suggest that in order to modify conversion at a fixed power, it is necessary to change the instantaneous power of a few orders of magnitude.

The different powers also lead to a different distribution of the products. The selectivity of the gaseous products for each mode, illustrated in Fig. 4, is shifted to

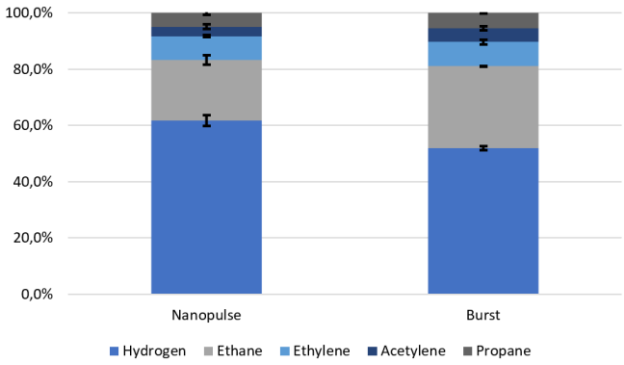

Fig. 4. Selectivity of the gaseous products for the two modes.

From the composition of the gas mixture exiting the system, it is possible to calculate the amount of carbon deposited in the reactor. For the nanopulsed mode, 22% of the injected carbon moles are turned into a solid, against 13% for the burst mode. This effect is reflected on the higher hydrogen selectivity of the nanopulsed mode: a greater proportion of the methane is decomposed and more carbon atoms do not recombine under the form of gaseous products. A global stoechiometric equation of the conversion of methane in both cases can be written for the burst (4) and nanopulsed (5) mode :

$$CH_4\,(g) \rightarrow 0{,}44\,H_2\,(g) + 0{,}25\,C_2H_6\,(g) + 0{,}07\,C_2H_4\,(g) + 0{,}04\,C_2H_2\,(g) + 0{,}05\,C_3H_8\,(g) + 0{,}13\,C(s) \quad (4)$$

$$CH_4\,(g) \rightarrow\ 0{,}59\,H_2\,(g) + \ 0{,}20\,C_2H_6\,(g) + \ 0{,}08\,C_2H_4\,(g) + \ \ 0{,}03\,C_2H_2\,(g) + \ \ 0{,}05\,C_3H_8\,(g) + \ 0{,}22\,C(s) \quad (5)$$

Relative error for all stoechiometric coefficients is below 10%, except for acetylene for wich it reaches 20% (due to its low concentration). These coefficients are re-calculated from the selectivity of the gaseous products to take the solid carbon into account.

The overall energy effiency is quite low. The energy necessary to convert one mole of methane is 10 000 (± 1000) kJ in the burst mode, and 8000 (± 200) kJ with the nanopulse mode. Energy efficiency for the conversion of one mole of methane, calculated on the basis of Equation 1, is around 0,8-0,9 %. Although the global efficiency of the reaction is currently limited in our reactor, the 20% increase in conversion when switching to the nanopulse generator points to the better yield associated with this type of discharge.

4. Conclusion

Methane was successfully converted to hydrogen and higher hydrocarbons. For a same average power, conversion and products selectivity was modified by the distribution of power along time by pulsing the discharge in two different modes. The change in instantaneous power is of two orders of magnitude. This study opens the door for further characterization of the discharge, especially diving deeper into the electrical characterization and variation of the parameters. In particular, an increase in power or a lower flow to observe greater conversion would be interesting to allow for the visualisation of trends. Optical emission spectroscopy would also allow for a better understanding of the discharge behaviour.

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