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Reforming of CH_4 and CO_2 by a nanosecond-pulsed discharge at atmospheric pressure

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Abstract: We investigated the dry reforming process assisted by a nanosecond pulsed discharge at atmospheric pressure. Reaction products have been characterized and related to the process parameters. A comparison to other plasma techniques is possible in terms of conversion and energy efficiency values.

Keywords: nanosecond pulsed discharge, dry reforming, syngas

1. Introduction

Carbon dioxide and methane are important greenhouse gases. In addition to their sequestration, the dry reforming process allows to convert them to value-added chemicals. If the process is sustained by green energy, then one can store solar energy in chemical energy, producing the so called ‘solar fuels’ [1]. Conventional thermal methods have many disadvantages, noticeably the easy deactivation of catalyst [2]. Techniques based on cold plasmas are a promising option, since they operate at low temperature, thus reducing thermal losses. In addition, plasma based systems are characterized by low inertia, and therefore are inherently quick-start devices, suitable for the consumption of excess renewable energy.

Dielectric Barrier Discharges have long been investigated, due to their simplicity and reliability. When CO_2 and CH_4 are the feed gases, DBDs produce syngas and light hydrocarbons, but also liquid oxygenates [3, 4] and liquid hydrocarbons [5, 6]. Unfortunately, both the conversion rate and the global energy efficiency are low. To overcome these limitations, the synergy between plasma and catalysis is actively explored at the present. A complementary route is to attempt different discharge configurations. Nanosecond pulsed discharge (NPD) are characterized by higher mean electron energies [7]. Thus one guesses higher dissociation rates too and eventually higher conversion and efficient values.

In the present paper, we report on preliminary results obtained by using a nanosecond pulsed discharge to activate a mixture of CH_4/CO_2.

2. Experimental setup and results

The experimental setup is shown in Fig. 1. The reactor is made of a quartz tube (internal diameter 10 mm, external diameter 13 mm), containing two brass discs (diameter 8 mm). The discharge in plane-to-plane configuration occurs up to a gap of 10 mm.

The discharge is sustained by a power supply (NPG-18/3500 (N), Megaimpulse Ltd.) triggered by a wave-form generator (WFG-Agilent 33220A, Agilent Technologies Inc.) and occurs between the two electrodes. The discharge current and voltage are measured by a Magnelab CT-D-1.0 probe and HVP Tektronix P6015A high-voltage probe, respectively. V/I signals were recorded by a digital oscilloscope (WaveSurfer 104MXs-A, LeCroy, 1GHz). The frequency is controlled by WFG and set in a range between 100 and 3000 Hz.

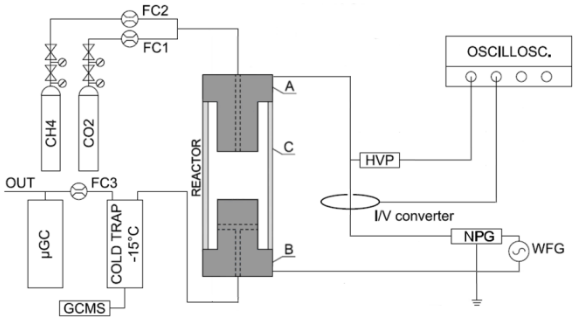

Fig. 1. Schematic representation of the experimental setup. A HV electrode; B grounded electrode; C glass tube reactor; HPV High Voltage Probe; NPG Nanosecond Pulsed Generator; WFG wave-form generator; FC mass flow controller.

The time delay introduced by probes, cables, and the oscilloscope is a source of systematic errors. This spurious phase shift between the measured values of voltage and current has been evaluated by reducing to zero the time integral of the product between the V and I values, both measured with the plasma switched off [8]. This last condition was obtained by filling the reactor with vapours of Freon-113. As an example, for a 6 mm gap the time delay was estimated 2.18±0.01 ns. The instantaneous power is calculated as the product VI taking into account the time delay introduced by the acquisition system. The pulse energy is then the time integral of the instantaneous power. Fig. 2 shows the recorded voltage and current signals. The instantaneous power and the pulse energy are also shown.

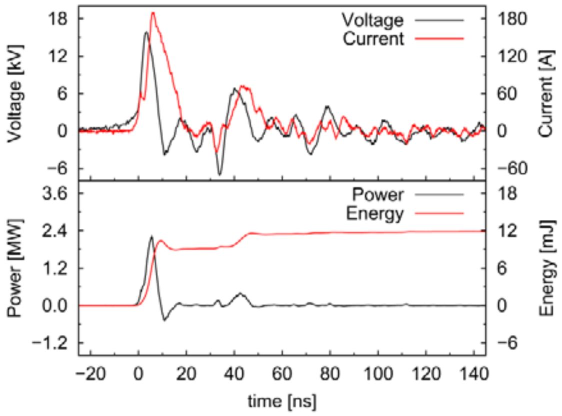

Fig. 2. Voltage, current, instantaneous power and energy for a 6 mm gap, 6.1 ns FWHM and 15.8 kV pulse.

Two mass flow controllers set the input flow, a third one records the output flow, after a cold trap a -15 °C.

On-line gas detection was performed by using an Agilent 3000 microGC. Helium, hydrogen, methane and carbon monoxide were measured by a Molesieve column with back-flush; carbon dioxide, ethane, ethylene, acetylene, propane and propyne by using a Plot U column. Standard compounds were used to calibrate the instrument. Liquid condensates were dissolved in acetonitrile and analysed using a Finningam Trace GC Ultra GC-MS. Water, the main by-product, was estimated by standard addition method, using a Carbowax column. Solid carbon was collected from the reactor wall and characterized by FTIR spectroscopy, XPS spectroscopy and scanning electron microscopy.

The conversion rate of the reactants (methane or carbon dioxide) is defined as:

$$C_{\mathrm{reac}}\ \% = \frac{n_{\mathrm{reac,conv}}}{n_{\mathrm{reac,input}}} \times 100. \qquad (1)$$

The specific energy input (SEI) is the average amount of energy injected in the plasma for each reactant molecule:

$$SEI\ [kJ/mol] = \frac{Power}{n_{\mathrm{reac,input}}}, \qquad (2)$$

where n is the molar flow (mol/s). We varied the SEI by changing the discharge frequency or the reactant flux.

In Fig. 3 the conversion rates as function of SEI are reported as example. The product selectivity as function of the process parameters will be present at the conference.

Following [9], the efficiency of energy conversion, *ECE*, is defined as the ratio between the energy contained in the products (LHV_{prod}), and the sum of the energy of the converted reactants (LHV_{reac}) with the energy injected in the plasma (E_{plas})

$$ECE\ \% = \frac{LHV_{prod}}{LHV_{reac,conv} + E_{plas}} \times 100 \qquad (3)$$

where LHV indicate the Lower Heating Value. *ECE* allows one to compare the efficiency of fuel production of different techniques. Fig. 4 shows ECE for the production of syngas as a function of SEI.

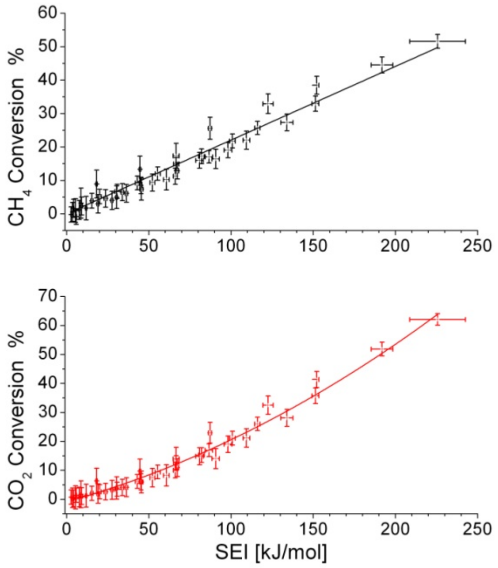

Fig. 3. Conversion rates as function of the SEI

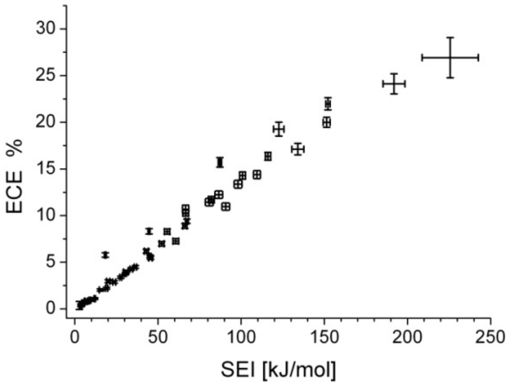

Fig. 4. ECE % for syngas production as function of SEI.

The efficiency increases if the energy content of the solid carbon is taken into account.

With respect to the DBD, we observe both a significant increase of the reactant conversion and a different branching ratio. In particular, NPD increases the selectivity towards ‘tail’ products, i.e. solid carbon and light gaseous chemicals (H_2, CO, C_2H_2) at the expense of liquid hydrocarbons and oxygenated compounds.

3. Acknowledgements

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4. References

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