I. INTRODUCTION

Nanosecond repetitively pulsed (NRP) discharges are being increasingly used in various applications, in particular for plasma-assisted combustion [1-3], nanomaterials synthesis [4], and aerodynamic flow control [5]. The key advantage of NRP discharges is their high-energy efficiency, and thus low power consumption, to produce highly reactive atmospheric pressure air plasmas. We seek to explore this property for water vapor dissociation. In this objective, water dissociation final products, i.e. H₂ and O₂ are measured and their production energy efficiency should be estimated and compared to other processes. A general overview of hydrogen production technologies [6] shows that besides commercial technologies such as partial oxidation and steam reforming processes, thermal and non-thermal plasma techniques could be considered as possible reforming technologies. Focusing on non-thermal plasma processes, different types of discharges were used to produce hydrogen from various liquid or gaseous fuels (mainly methane, natural gas and biogas), such as glow discharge, corona discharge, dielectric barrier discharge, microwave discharge and radio frequency discharge [7, 8]. On the other hand, water dissociation using non-thermal plasma technique was previously investigated, mainly in Russia, as reported by Fridman [9], using low and moderate pressure microwave discharges at high specific energy (1-4 kJ/L), and to a lower extent, low pressure glow discharges. The energy efficiency was found to decrease with gas pressure (from 0.05 to 0.4 atm). The initiation reactions claimed by authors for water vapor dissociation are dissociative attachment and dissociation of vibrationally excited molecules

\[ \text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H}_2\text{O}^* \]

\[ \text{H}_2\text{O}^* + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH} + \text{H}_2\text{O} \]

These mechanisms correspond to major paths of energy transfer for relatively low reduced electric field (E/N) conditions (lower than 80 Td).

From a simulation using inelastic electron-molecule collision cross-sections, the channels of energy transfer from electrons to water molecules can be established [9]. This calculation was performed using Bolsig+ [10] with the cross-section database of Morgan [11] for the case of pure water vapor at 400K and atmospheric pressure. The results are presented in Fig. 1 for a reduced electric field (E/N) ranging from 1 to 1000 Td. As can be seen, increasing the E/N over 80 Td leads to a shift of the conversion of electrons energy from vibrational excitation to dissociation

\[ \text{e}^- + \text{H}_2\text{O} \rightarrow \text{e}^- + \text{H} + \text{OH} \]

and ionization.

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**Abstract**—Experimental study of a Nanosecond Repetitively Pulsed (NRP) discharge in atmospheric pressure water vapor at 450K is reported. The discharge is produced between two pin electrodes by application of voltage pulses (0-15 kV amplitude), 10 ns in duration, with a repetition frequency up to 30 kHz. Electrical measurements were done to determine the energy deposited in the discharge. The energy per pulse ranges from 1 to 10 mJ. In order to determine the efficiency of water vapor dissociation, the concentration of the final reaction products (H₂ and O₂) and their respective flow rates were measured.

**Keywords**—NRP discharge, atmospheric pressure, water vapor dissociation

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Fig. 1. Energy deposited by electrons in pure water vapor at 1 atm and 400K, using Bolsig+ [7] with Morgan’s database [8].
The objective of this work is thus to evaluate the energy efficiency of water dissociation using the NRP discharge in a 100-1000 Td reduced field range in pure water vapor at atmospheric pressure.

II. EXPERIMENTAL SETUP

A. Gas Flow Setup

The experimental setup (Fig. 2) consisted of a water vapor generator without carrier gas, a reactor where the plasma discharge was generated, and a cold-trap that re-condensed the water vapor. The exhaust gases went through a mass flow meter and reached the gas chromatograph (GC) injection valve, thus allowing online gas analysis.

The gas flow setup (Bronkhorst) was composed of 3 modules: a regulation system, a heater and a closed loop temperature control. The input of liquid water was regulated at a flow rate of 200 g/h in this experiment. A heater vaporized the water to produce a flow of pure water, without carrier gas. The water tank was pressurized with helium at 4 bar.

The flow of pure water vapor was transferred to the reactor through a heated line. The line temperature was set at the vapor temperature, i.e. 450K in this experiment. The reactor was made of an electrically grounded steel tube (4 cm inner diameter) heated to 450K. The total volume of the reactor was 120 cm³. The discharge was generated in this tube, between two pin electrodes (insulated from the steel tube) placed perpendicular to the gas flow. The gas flow velocity at 200 g/h was 0.1 m/s in the discharge zone. Two quartz windows mounted on the reactor walls allowed optical access to the discharge zone.

The reactor outlet line was connected to a cold trap at 273K that condensed the water vapor. A mass flow meter (full scale 100 mL/min) connected at the cold trap outlet measured the total flow rate of all the gases that do not condense.

The chemical species concentrations were then measured using an Agilent 6890A gas chromatograph with a Restek 100/120 Shincarbon ST 2 m × 1 mm micro-packed column and a thermal conductivity detector. Argon was used as carrier gas.

B. Plasma Production Setup

The NRP discharge setup and the electrical measurement system are sketched in Fig. 3. NRP discharges were generated between two tungsten pin electrodes (2 mm diameter), in a pin-to-pin configuration, separated by an adjustable gap distance ranging from 1 to 10 mm. A pin was grounded while the other one was stressed by high voltage pulses of 10 ns duration, 1-30 kHz pulse repetition frequencies (PRF) and 0-15 kV amplitude. High voltage pulses were obtained using a solid state pulse generator (FID Technologies FPG 10-30MS). The NRP discharges were produced in pure water vapor at atmospheric pressure.

Fig. 2. Schematic diagram of the gas flow setup.

Fig. 3. Schematic diagram of the electrical setup.

Fig. 4. Voltage and current typical waveforms.

The voltage applied across the electrodes gap was measured with a 1:1000, 100 MHz bandwidth high-voltage probe (LeCroy PPE20kV). The current was measured with a Pearson coil current monitor (Model 6585) connected to a low-voltage attenuator (Barth Model 2-20). Both signals were recorded simultaneously with a 1 GHz LeCroy Wavepro7100 oscilloscope.

In Fig. 4 are presented typical voltage and current waveforms. The energy deposited in the discharge was deduced from the instantaneous product of the two waveforms. The delay between the two signals was compensated to take into account the time response of...
the probes and the cables length. After the voltage pulse, voltages oscillations occur because of non-matched reflections. No discharges were observed during these oscillations.

III. METHODOLOGY

The first step was to identify the various accessible regimes for a NRP discharge in pure water vapor.

With a fixed set of parameters, the focus was placed on the gas characterization. Prior to the experiments, the gas line connecting the reactor outlet to the GC injection port (through the cold trap and the mass flow meter) was first purged of air using argon (carrier gas for the GC). It is important to mention that during operation, the total amount of water vapor was re-condensed in the cold trap. The flow rate measured at the cold trap outlet was solely due to gas production (analyzed using GC) initiated by water dissociation (this flowrate is small compared to the reactor inlet water vapor flow).

IV. RESULTS

A. Discharge Regimes

The regimes of operation of the NRP discharge in water vapor were studied as a function of the pulse repetition frequency, inter-electrode distance, gas temperature and applied voltage. The results of the regimes available as a function of the distance and the applied voltage are presented in Fig. 5. These results were obtained at a PRF of 30 kHz and with water vapor at a temperature of 450 K and flow of 0.15 m/s.

From 2 mm to 8 mm inter-electrode gap distance, the corona onset voltage remains approximately constant (∼6-7 kV). For small inter-electrode distances, the corona regime is unstable and transient transitions to spark regime are observed. For larger discharge gaps, the spark regime occurs for an electric field of about 20 kV/cm. A narrow region appears for gaps larger than 5 mm with another regime. It starts with two coronas, tending to fill the whole gap. Additional measurements are needed to confirm that this discharge regime is similar to the glow regime as defined by Pai [12]. However, the regime here chosen was the spark regime [13], which is more stable than the glow regime in these experiments, and leads to a greater energy deposition into the gas. The discharge gap was fixed at 5 mm.

A preliminary study of the discharge was done by Optical Emission Spectroscopy (OES) in the UV-Visible range. Fig. 6 shows the emission intensity from 250 to 850 nm in the center of the discharge. The signal is integrated over 5 ms, which correspond to 50 pulses at 10 kHz pulse repetition frequency. Strong emission from atomic hydrogen is measured: the Hα intensity is 60000 and Hβ is 10000. Atomic oxygen and OH also have strong emission, which suggests that a time and/or space resolved study would be interesting in the near future.
under these conditions (Fig. 6).

It is also important to note that the gas composition was taken into account in order to correct the flow outputs (Table I) for each gaseous species. Table I shows that only minor corrections were required, as all the major gases measured have a correction factor close to 1.

Results are presented in Fig. 7, where it can be verified that the 2/3 H₂ and 1/3 O₂ gas composition is in agreement with the theoretical ratio and confirms pure dissociation of water.

It should also be mentioned that using a colorimetric method, H₂O₂ was not detected in the condensed water, probably because of the relatively high temperature of the condensed water (~ 60°C).

In these conditions, assuming that the hydrogen flow (3.1 mL/min) corresponds to the water flow dissociated, it can be estimated that 0.04% of the inlet water vapor was dissociated. This result could be expected since the discharge (5 mm length × approx. 1 mm diameter) represents only 0.4% of the reactor cross-section. The fraction of dissociated water is not a relevant performance criterion in these conditions and so the hydrogen formation energy cost will be used for further analysis.

C. Energy cost considerations

After stabilization of the water dissociation products formation, the energy deposition was progressively raised to 47, 64, and 81 W (i.e. from 110 to 440 J/L). For each operating condition, a steady state was reached, corresponding to an increase of the total flowrate (for which GC measurements were performed), and the hydrogen production was then measured as a function of the discharge input power. Fig. 8 shows the dependence of the H₂ production with input power.

From these results, the energy efficiency could be estimated (Fig. 9). A maximal value of 0.85 g-H₂/kWh was obtained.

The usual values of energy efficiency for high purity hydrogen using electrolysis are in the range 12-20 g-H₂/kWh; 20 g-H₂/kWh corresponds to 80% of the maximum thermodynamic efficiency. The observed energy efficiency is then low compared to these reference values. Furthermore, the slope of the curve in Fig. 8 indicates that there is more energy loss in other processes than H₂ formation when the energy deposited increases.

Assuming a gas temperature between 450 and 2000K in the discharge column, and assuming \( E = \frac{V}{d} \) (d: inter-electrode gap distance), which was shown to be valid for the spark regime [13], the calculated E/N values range from 200 to 850 Td in these conditions. Thus the spark discharge regime does not appear to be the most suitable regime for effective water dissociation.
V. CONCLUSION

These experiments of NRP discharges in pure water vapor at atmospheric pressure show that hydrogen and oxygen are produced with a molar ratio corresponding to water dissociation. Among the various regimes available, we have chosen to focus on the spark regime (high E/N). By measuring the power consumption and the hydrogen production using this discharge, we have shown that the energy efficiency of spark discharges is at least one order of magnitude lower than that of industrial processes (specifically electrolysis) and also lower than low pressure microwave discharges [9]. Rather than decreasing the water vapor pressure, the next step will be to decrease the reduced electric field. Corona and glow discharge regimes in water vapor at atmospheric pressure will be investigated.

REFERENCES