Investigating the dry reforming reaction in a ns-pulsed discharge plasma

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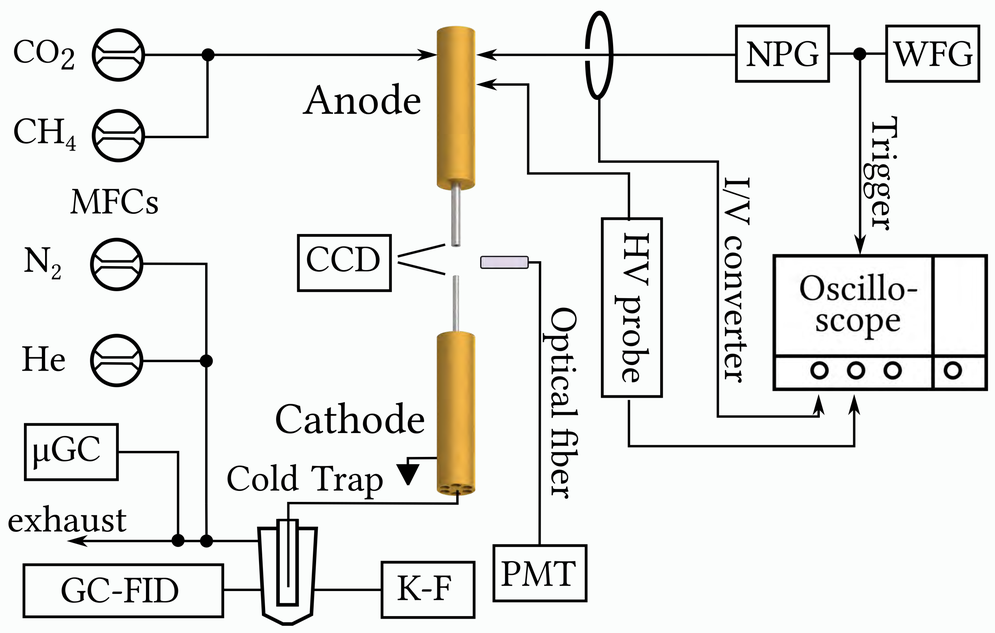
Abstract

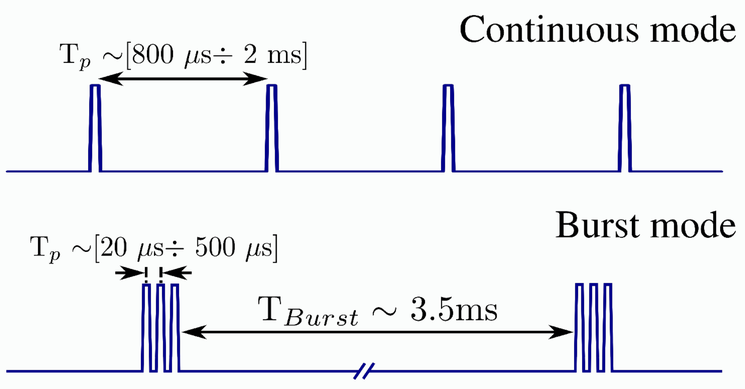
Methane emissions have increased in the past decade, with a substantial contribution from the agriculture, waste, and fossil fuel sectors. [1] The dry reforming of methane (DRM) reaction converts one molecule of CH_4 and one of CO_2 into syngas, a value-added gaseous mixture of carbon monoxide and hydrogen. Still, this process struggles to become a mature industrial technology, mainly because of its low energy efficiency and catalyst deactivation at high operating temperatures. Among non-thermal plasmas, the pulsed nanosecond discharge is gaining growing attention as one of the most energy-efficient ones to promote chemical reactions, taking advantage of the high electron densities and electron energies that can be reached out of thermal equilibrium. The study of the effects caused by changes in the discharge's pulsing scheme is being proven to be a tool to increase efficiency and to control selectivity. In the plasma-driven CO_2 splitting, Montesano et al. [2] showed that conversion and efficiency increased by shortening the time between successive discharges for the same total energy. Below 100 μs, subsequent pulses do not act independently but occur in an environment perturbed by the initial pulse. The same phenomenon is here investigated for the DRM reaction. [3]

Experimental Set-up and Methods

Pin-to-pin configuration discharge: The high voltage (HV) electrode is a tungsten tube, which also acts as inlet gas line; The grounded electrode is a tungsten rod;The inter-electrode gap set at 5 mm.



The HV generator (NPG 18/100k, Megaimpulse Ltd.) produces pulses with FWHM $\sim$ 10 ns and rise time < 4 ns. The trigger is provided by a waveform generator (32250A, Agilent Technologies Inc.).
Applied voltage V(t) and current I(t) are measured by a HV probe (P6015A, Tektroniks) and an I/V converter (CT-D1.0, Magnelab). A digital oscilloscope (WaveSurfer 104MXs-A, LeCroy) is used to record I(t) and V(t). A phototube (H10721-210, Hamamatsu) detects the discharge's optical emission, while a CCD camera is used to imaging the discharge.

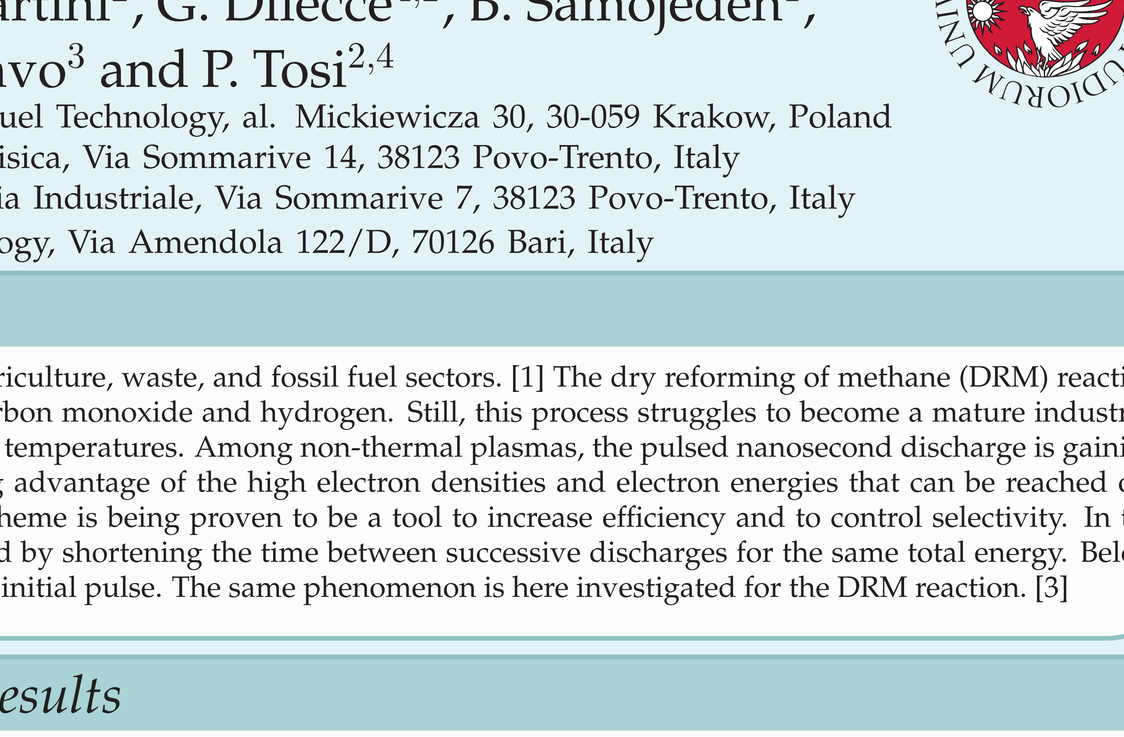


Two different pulsing schemes:

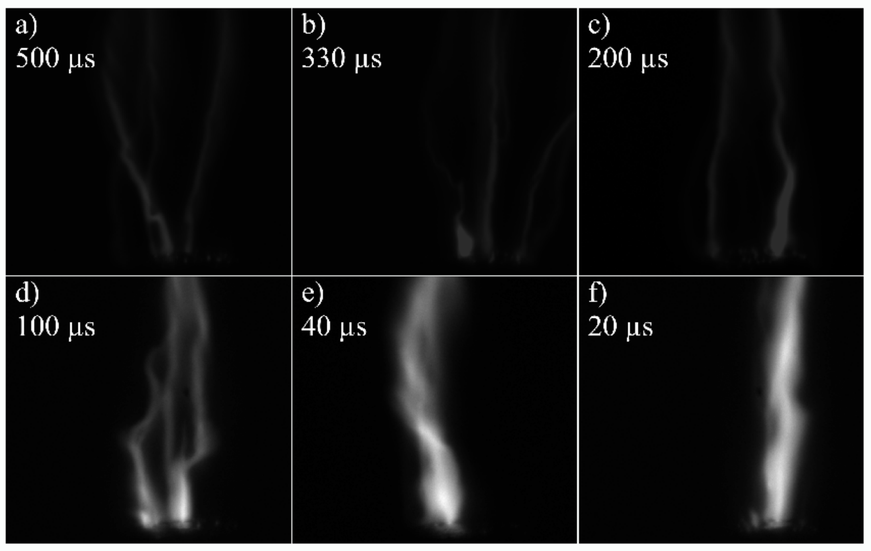
- **continuous mode**: a constant repetition of equally spaced pulses, frequency 450 – 1200 Hz.
- **burst mode**: few, much closer pulses (frequency 2 - 50 kHz) grouped into repetitive bursts of 300 Hz frequency.

Results

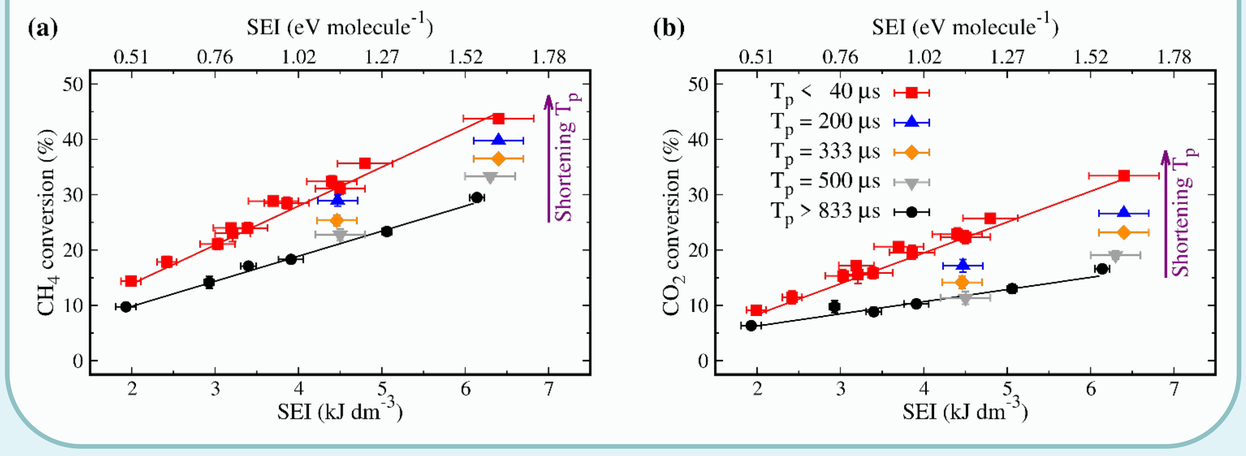
Burst pulses are different from each other under a certain T_p threshold. The first one is similar to the ones in continuous mode. The successive show lower voltage and higher current. The different gas composition encountered by the second pulse is likely to modify the discharge impedance.



The images of a three-pulse burst are shown below. From 100μs up to 500 μs, each pulse is spatially independent; for shorter inter-pulse times, 20 and 40 μs, the second and third discharges appear to follow the same path.



The conversions of CH_4 and CO_2 are affected by the change in T_p. At each SEI, the dissociation values increase by shortening the inter-pulse time.



Conclusions

- The dry reforming reaction in an NRP discharge was investigated for different inter-pulse times;
- The reactant conversion and energy efficiency increase by shortening T_p, with saturation below 40 μs;
- product selectivity is also dependent on the inter-pulse time, with closer HV pulses bolstering CO and H_2;
- increased performance could be due to a progressive modification of the discharge conditions, both for the gas composition and the load impedance;
- Pulses following the first are characterised by a comparatively lower breakdown voltage and a larger current;
- after a T_p threshold, the distinct discharge paths collapse into a single channel.

Acknowledgements

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References

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