

# Conversion of CH<sub>4</sub> to CO and oxygenates from model exhaust gases by discharges of streamer-to-spark transition type.

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**Abstract:** We investigated a conversion of CH<sub>4</sub> into oxygenates or CO by a transient spark discharge operating above water in N<sub>2</sub>/CO<sub>2</sub>/CH<sub>4</sub> mixtures at atmospheric pressure. The emission of N<sub>2</sub>(C), N<sub>2</sub>(B), N<sub>2</sub><sup>+</sup>, CN, CH, C<sub>2</sub>, OH, NH, N, O, H, and C species was detected by emission spectroscopy. Gaseous products detected by infrared spectroscopy were CO and acetylene. Methanol and acetaldehyde were identified in the liquid phase.

**Keywords:** plasma reforming of methane, discharge above water, oxygenates

## 1. Introduction

Atmospheric pressure plasmas in air generated by electrical discharges present considerable interest for a wide range of environmental applications, such as air pollution control or waste water cleaning. New types of discharges are therefore still being developed and studied, with a focus on efficiency, power requirements, stability, reliability and simplicity. For this reason we investigated a novel type of streamer-to-spark atmospheric pressure transition discharge, named the transient spark (TS) in air [1-2] and N<sub>2</sub>/CO<sub>2</sub>/CH<sub>4</sub> mixture above water surface. This mixture represents simplified exhaust gases produced by the pyrolysis of organic waste by natural gas combustion gases [3]. The goal of this preliminary study was to test the applicability of TS for the conversion of residual CH<sub>4</sub> into oxygenates (partially oxidized hydrocarbons) and CO/H<sub>2</sub>.

## 2. Experimental set-up

The experiments were carried out at room temperature in atmospheric pressure with the gas flow 0.2-0.7 l/min. The concentration of CH<sub>4</sub> (from natural gas with 95-96

vol. % of CH<sub>4</sub>) in the buffer N<sub>2</sub>/CO<sub>2</sub> mixture (1:1) varied from 0 to 25 vol. %. Water was directly present in the discharge chamber: the low voltage planar copper electrode was submersed. A stainless steel needle was used as a high voltage electrode. The distance between the HV electrode and the water surface varied from 4 to 6 mm. The total electrode's gap was 10 mm.

A DC high voltage power supply connected via a series resistor ( $R = 1.64 - 9.84 \text{ M}\Omega$ ) was used to generate a positive TS discharge. The discharge voltage was measured by the high voltage probe Tektronix P6015A and the discharge current was measured using the current probe Pearson Electronics 2877 (1V/A), both linked to the 200 MHz digitizing oscilloscope Tektronix TDS2024. The experimental set-up is depicted in Fig. 1.

The UV-VIS spectra were obtained by an optical system leading to a two-channel emission spectrometer Ocean Optics SD2000 (200 – 1100 nm). The infra-red (IR) absorption spectroscopy was used for the analysis of gas samples. The liquid samples were then analyzed by Proton-Transfer-Reaction Mass Spectrometry (PTR-MS).

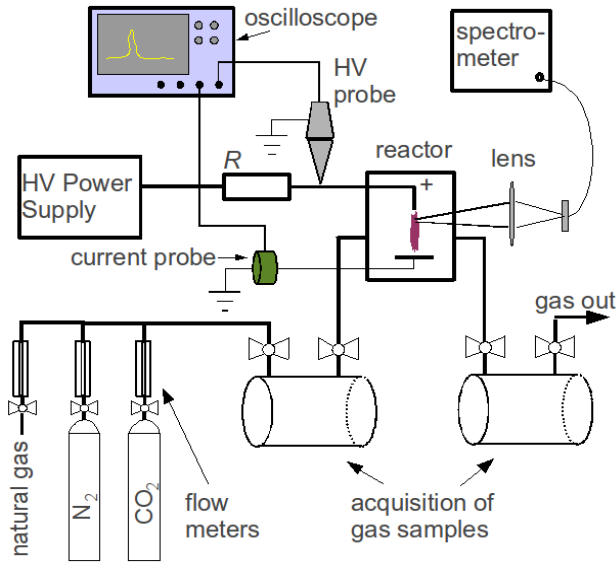


Fig. 1 Schematic of the experimental set-up,  
HV - high voltage,  $R$  – resistor.

### 3. Transient spark

TS is a filamentary streamer-to-spark transition discharge initiated by a streamer, which transforms to the short spark pulse due to the discharging of an internal capacity of the discharge chamber ( $C_{int}$ ).

When  $C_{int}$  is discharged, the current reaches a high pulse ( $\sim 1$ A) and the voltage drops to zero due to the fall on the external resistance  $R$ . Then, during the quenched phase,  $C_{int}$  is recharged by a growing potential on the stressed electrode. Usually, during this relaxation phase when the gap potential crosses a specific threshold, there appears a corona discharge in its glow regime, and some pre-breakdown streamers. Figure 2 shows typical waveforms of a TS pulse, together with the calculated power. The streamer preceding the TS pulse is also visible.

As soon as  $C_{int}$  is charged enough again, it triggers a new pulse. This process repeats with a typical repetitive frequency of 0.5-15 kHz. As  $f$  increases, TS may transform to a pulse-less glow discharge regime [3], with a constant current above 1 mA. This transition is controlled by the external resistance  $R$ , the distance between electrodes, and the gas flow.

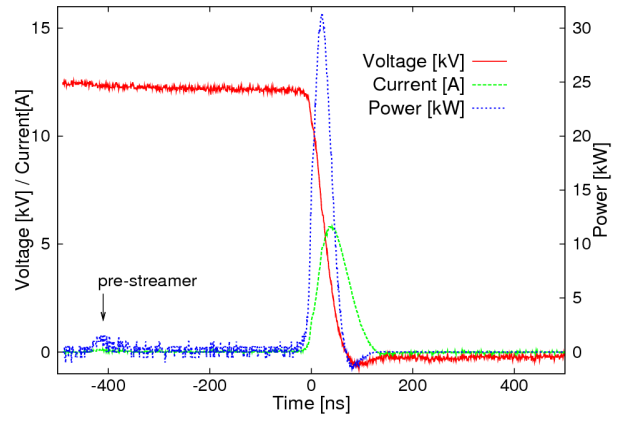


Fig. 2 Typical TS waveforms and calculated power.

### 4. Results and Discussion

When a high voltage  $U_o$  applied to the stressed needle electrode was progressively increased, we first observed a streamer corona. As a threshold voltage for TS was achieved, a transition to TS occurred at the discharge voltage  $U_{dis}$ . Further increase of  $U_o$  led to a monotonous increase of TS frequency  $f$ .

The increase of  $f$  first led to slight increase of  $U_{dis}$ . However, from about 4 kHz, the value  $U_{dis}$  started to decrease and the frequency became less stable. With the same  $U_o$ , the discharge can operate with several different values of  $f$ . This was related to the appearance of pulses with different value of  $I_{max}$ . Smaller pulses appear at lower value of  $U_{dis}$  and so repeat with a higher frequency than larger ones. TS can randomly switch between these two types of pulses. However, as the average frequency continued to increase with  $U_o$ , the small pulses started to dominate. This led to the further decrease of  $U_{dis}$ , but in the studied range of  $U_o$ , up to 20 kV, the transition to the stable glow discharge regime did not occur for  $R > 4.9$  M $\Omega$ .

The decrease of  $U_{dis}$  at  $f > 4$  kHz caused the decrease of energy per pulse delivered to the gap, but it was compensated by the increase of  $f$ . As a result, the values of  $I_{mean}$  and input power  $P_{in}$  grew almost linearly with  $f$  up to 3 mA and 13 W, respectively.

We found that the decrease of  $U_{dis}$  at high frequencies was accompanied by a significant differences between the obtained emission spectra. At 2 kHz, CN emission dominated over  $N_2$  2<sup>nd</sup> positive system, and atomic lines (C, N, O, H) were clearly visible, whereas at 9 kHz, atomic lines almost disappeared and  $N_2$  1<sup>st</sup> and 2<sup>nd</sup> positive systems dominated in the spectra. The emission of  $N_2^+$  1<sup>st</sup> negative, OH (A-X), NH (A-X),  $C_2$  Swan and CH systems were also observed in spectra (Fig. 3 and 4) and they were also more intense at lower frequencies.

Thanks to the very short spark pulse duration, the plasma generated by TS cannot reach LTE conditions. This was confirmed by vibrational ( $T_v$ ) and rotational temperatures ( $T_r$ ) calculated by fitting the experimental spectra of  $N_2$  2<sup>nd</sup> positive system with the simulated ones (we used Specair program [12]). The presence of atomic lines indicates even much higher temperature of electrons ( $T_e$ ).

The  $T_r$  grew from approximately from 500 to 1500 K as the frequency increased from 1 to 14 kHz. There was no clear dependence of  $T_r$  (3000-4000 K) on  $f$ . The increase of  $T_r$  indicates that the plasma generated by TS approaches LTE conditions with increasing  $f$ .

The decrease of emission intensity of atomic lines with growing  $f$  may also indicate decrease of  $T_e$ , resulting to slower electron impact reactions and thus also weaker chemical effect of TS discharge. On the other hand, the increase of  $T_r$  can certainly accelerate many chemical reactions between reactive species produced by electron impact reactions. As a result, the influence of  $f$  and different TS regimes on induced plasma chemistry is uncertain.

Indeed, we observed that the only relevant parameter influencing the efficiency of  $CH_4$  conversion were specific input energy ( $E_s$  [J/l]) and the initial concentration of  $CH_4$  ( $c_{CH_4}$  [vol. %]). At a fixed specific input energy  $\sim 500$  J/l, an exponential decrease of  $CH_4$  removal rate from around 65 to 10 % was observed, as the initial concentration of  $CH_4$  increased from 0.5 to 25 vol. %.

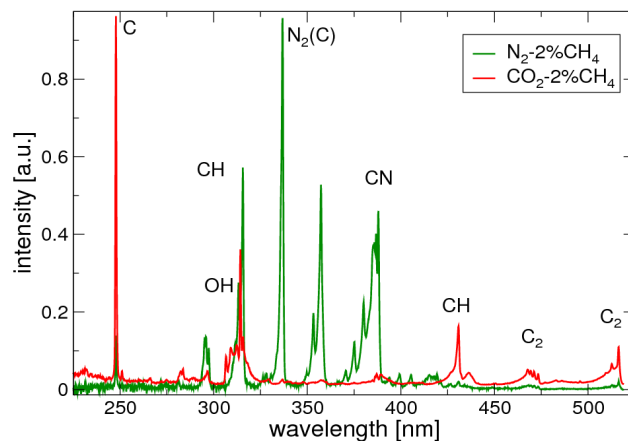


Fig. 3 Typical TS UV spectra,  $f \sim 3$  kHz.

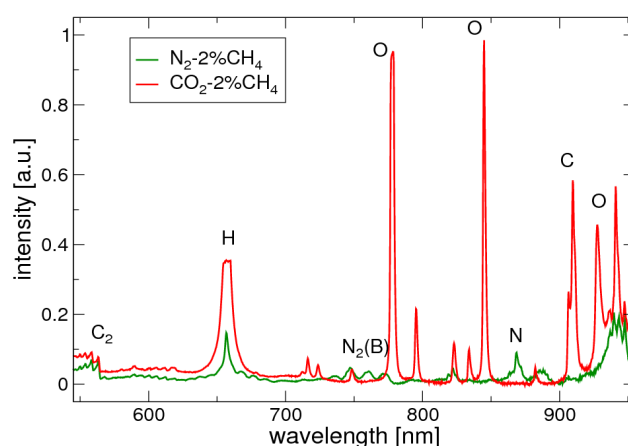


Fig. 4 Typical TS VIS spectra,  $f \sim 3$  kHz

However, the absolute amount of removed  $CH_4$  ( $\Delta c_{CH_4}$  [vol. %]) increased from about 0.5 to 2.5 vol. % (Fig. 5). The amount of energy which had to be delivered to the discharge gap to remove 1  $CH_4$  molecule was relatively low, it decreased exponentially with increasing  $c_{CH_4}$  from approximately 33 to 5 eV.

The chemistry of the  $CH_4$  conversion in the studied mixture is certainly very complicated, with many possible products. The major gas phase product is CO. Figure 6 shows the concentration of produced CO ( $c_{CO}$ ) and a selectivity of  $CH_4$  to CO conversion ( $100 \times c_{CO} / \Delta c_{CH_4}$ ) as a function of  $c_{CH_4}$  at a fixed  $E_s \approx 500$  J/l. After initial increase, there is a slight decrease of CO concentration with further increase of  $c_{CH_4}$  resulting into the decrease of  $CH_4$  to CO conversion selectivity. If we assume that there are

two dominant CH<sub>4</sub> removal channels: to CO and to organic species, this indicates that the conversion to CO is much faster. However the amount of reactive oxygen species required for CH<sub>4</sub> to CO conversion is limited, because their production from CO<sub>2</sub> not very efficient. This conversion channel becomes therefore saturated at higher  $c_{CH_4}$ , and the conversion of CH<sub>4</sub> to oxygenates may dominate, since these processes certainly require less reactive oxygen species.

The PTR-MS analysis showed several dozens of possible organic species accumulated in the liquid phase. However, the identification of all produced organic species requires further research. The most probable are methanol and acetaldehyde as dominant products in the liquid phase and acetylene detected in the gas phase at higher  $c_{CH_4}$ .

## 5. Conclusions

This preliminary results show that TS represents a relatively simple and efficient possibility for the generation of highly reactive plasma by a DC power supply. Thanks to the very short spark pulse duration (~100 ns) the plasma cannot reach LTE conditions. On the other hand, the periodic streamer-to-spark transition provides non-equilibrium conditions with fast electrons resulting in generation of many reactive species (C, N, O, H, CN, N<sub>2</sub><sup>\*</sup>, CH, OH, C<sub>2</sub>, ...). This leads to the conversion of CH<sub>4</sub> to CO and/or other organic species at relatively low energy cost. However, the optimization of these processes with respect to the conversion selectivity towards organic species and the identification of all major organic species requires further research.

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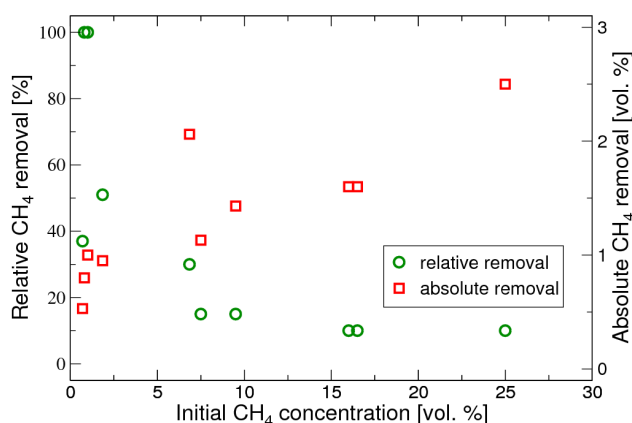


Fig. 5 Relative and absolute CH<sub>4</sub> removal rate as functions of initial CH<sub>4</sub> concentration,  $E_d = 500$  J/l.

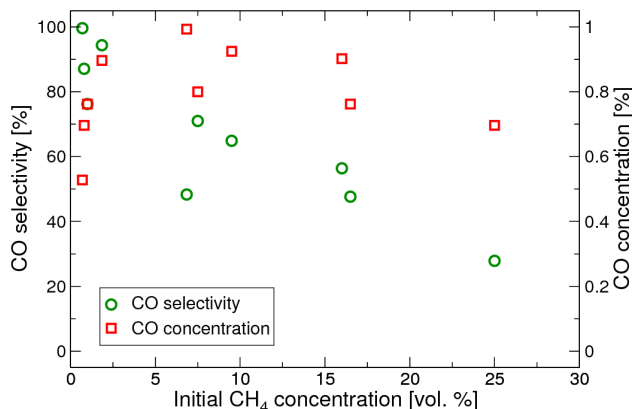


Fig. 6 Concentration of produced CO and selectivity of CH<sub>4</sub> to CO conversion as functions of CH<sub>4</sub> concentration,  $E_d = 500$  J/l.

## References

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