# $CO_2$ conversion in a pulsed surfaguide microwave plasma at atmospheric pressure

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**Abstract:** In present work, $CO_2$ conversion in plasmas sustained with ultrafast microwave pulsations was investigated at atmospheric pressure. With time-resolved optical emission spectroscopy the evolution of the vibrational and rotational temperatures of in-reactor plasma has been observed at nanosecond time scale. The energy efficiency of $CO_2$ splitting and $CO_2$ conversion rate in pulsed mode are compared to continuous wave operation of the microwave source.

**Keywords:** $CO_2$ conversion, microwave plasma, pulsed microwave, energy efficiency.

## 1. Introduction

Rapidly growing renewable energy capacity, primarily from wind and solar energy, offers significant prospects for phasing out fossil fuels and decarbonizing the economy. Yet, the intrinsic intermittency of that sources calls for technologies able to store excess energy produced during one period and save it for another [1]. One of most efficient storage of surplus electrical energy is utilizing it for synthesizing liquid fuels. As compared to other types of energy storage technologies, like flywheels, batteries or compressed air storage, the energy stored in liquid fuels enables the highest storage capacity (in terawatt-hours range) and the longest discharge time (in range of years) [2]. One of the most attractive pathways is an endothermic reduction of carbon dioxide (eq. 1) which being captured from industrial exhausts may help to mitigate the green-house effect on the earth.

$$CO_2(g) \rightarrow CO(g) + 1/2O_2(g) + 283\ kJ/mol \qquad (1)$$

From another hand, the activation and deactivation of conventional chemical reactors are often too slow to follow the natural fluctuations in wind and solar power. Plasma-based reactors allow the process to be switch on or off almost instantaneously, and therefore are well compatible with an intermittent availability of electricity [3]. Among different plasma-based reactors, microwave plasma reactors so far demonstrated the highest efficiency (above 80 %) for conversion of $CO_2$ into CO at low-vacuum conditions [4, 5]. However, for future large-scale deployable technology for $CO_2$ conversion a vacuum operation is not desirable. Atmospheric pressure plasma systems are much more welcome for industrial scale applications, but the efficiency of the process degrades because much of the supplied energy is wasted through excessive heating of the gas. A promising solution was found in recent experiments by supplying the microwave energy in short pulses rather than continuously [6]. With a modulation time comparable with or faster than energy transfer time from electrons to translation energy of $CO_2$ molecules, the efficiency of CO2 splitting at atmospheric pressure in a compact coaxial torch was found to be promoted [6]. Given that the thermal mechanism appears to dominate the $CO_2$ dissociation at atmospheric pressure, fine control of the gas temperature with ultrafast pulsation of microwave energy looks as a promising tool.

## 2. Experimental

In present work, fast pulsation of microwave energy has been applied to sustain an atmospheric $CO_2$ plasma in a surfaguide [7] microwave reactor (Fig. 1). Advanced microwave generators developed on the basis of solid-state amplifiers with an output power of up to 8 kW were used for the experiments. They feature an independent control of pulse time ($t_{on}$) and interpulse time ($t_{off}$) in the range 50 ns to 100 µs, as well as the frequency within the range 2.4−2.5 GHz.

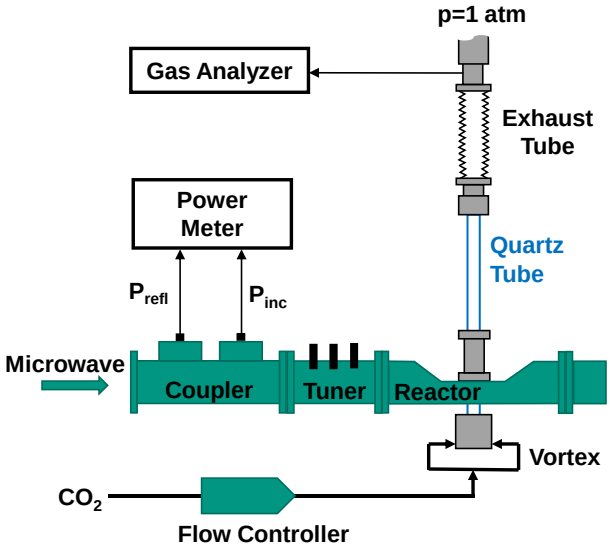


Fig. 1. Scheme of $CO_2$ conversion experiment in microwave plasma reactor (surfaguide) at atmospheric pressure.

To monitor plasma temperature along discharge parameters an optical emission spectroscopy (OES) with a nanosecond time gate was utilized. The emitted light from the centre of plasma reactor (see Fig. 2) is collected with a small collimating lens (4 mm in aperture) and guided by an optical fiber to the entrance of the high-resolution spectrograph Acton SP-2756 with 750 mm focal length. The light spectrum is acquired by an intensified (ICCD) CCD camera from Andor type A-DH340-18U-03 with a time gate < 2 ns. The spectrometer in that configuration provides a spectral resolution of about 25 pm. The synchronization of the ICCD camera gate with microwave pulsations provides precise in-phase accumulation of emitted light and enables time resolution down to several tens of nanoseconds.

The absorbed microwave power in the plasma was estimated from incident and reflected powers measured with a fast power meter. Reaction products were measured with gas analyser and the $CO_2$ inflow rate was controlled with a mass-flow controller (Fig. 1).

To determine the rotational and vibrational temperatures in the investigated plasma discharge, the molecular bands are fitted with synthetic spectra by utilizing the software MassiveOES [8, 9]. The fitting is performed by using of the database for the $C_2$ $d^3\Pi_g - a^3\Pi_u$ Swan band system by Brooke et al. [10], which was included into MassiveOES after careful evaluation [11] The fitting is performed under the assumption of a Boltzmann distribution which is justified for the present conditions [11].

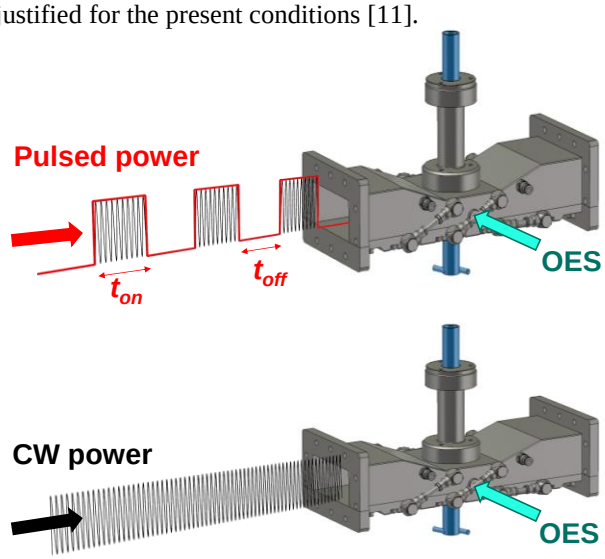


Fig. 2. Scheme of pulsed versus continuous wave (CW) supply of microwave energy in plasma reactor. Position for acquisition of emitted light for OES diagnostic shown with an arrow.

## 3. Results

The first ignition of plasma is enabled through micro-discharge initiated by applying high voltage to electrodes at outside surface of reactor quartz tube. The ignition occurs in pure argon flow and power > 1.8 kW. After that the argon is replaced with pure $CO_2$ gas and plasma column expands above the reactor (Fig. 3).

The plasma rotational and vibrational temperatures measured in pulsed operation were compared with results obtained in continuous wave (CW) operation (Fig. 2). For that purpose, the absorbed microwave power in CW mode was chosen to be close to the mean absorbed power in pulsed mode. One of the results for such a comparison is presented in Fig. 4, where pulse time ($t_{on}$) and inter-pulse time ($t_{off}$) were 5 and 10 microseconds, respectively. The input $CO_2$ flow was kept as high as 26.0 standard litre per minute (slm). In CW mode, the incident and reflected power were measured as high as 1460±150 W and 160±40 W, respectively. In pulsed mode, the measured peak (power within pulse) incident power was 4200±100 W and reflected one 440±15 W. Thus, the absorbed mean powers in CW and pulsed mode were quite close: 1300 W and 1260 W, respectively. The time resolution defined by ICCD camera gate was 100 ns.

Estimated $T_{rot}$ and $T_{vib}$ in CW scenario, have amounted to 6100±100 K and 7900±100 K, respectively. In pulsed mode, both $T_{rot}$ and $T_{vib}$ are modulated with the period of microwave pulsation and amplitude of about 9% and 6%, respectively. The temperature rising and falling intervals are of the order of $t_{on}$ and $t_{off}$ times. Interestingly, both $T_{rot}$ and $T_{vib}$ in pulsation mode are higher than ones in CW mode. This might originate from difference in temperature profiles of plasma in CW and pulsed mode.

## 4. Outlook

Further plasma scenarios with different $t_{on}$ and $t_{off}$ times and duty cycles are investigated and correlated with measured rotational and vibrational temperatures of plasma as well as with $CO_2$ conversion rate.

## 5. Acknowledgements

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Fig. 3. $CO_2$ atmospheric plasma in surfaguide reactor.

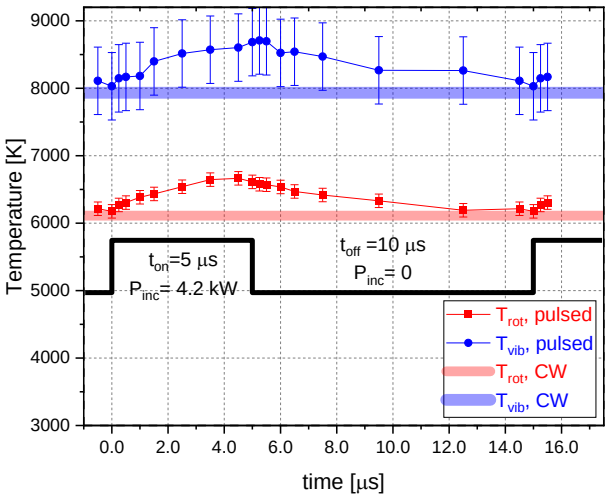


Fig. 4. Pulsed versus continuous wave (CW) operation. Incident microwave power pulse-form for pulsed mode is shown schematically with thick black line. Discharge parameters: p=1 bar, $CO_2$ inflow =26.0 slm

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